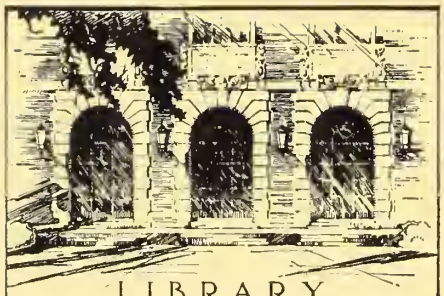

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1964-65

A STUDY OF ISOPOLYANIONS IN AQUOUS SOLUTION

Wilfred H. Nelson June 16, 1964

I BACKGROUND

Recently there has been some interest in the isopolyanions formed in aquous solutions of the transition metals, primarily with Group V-B and VI-B elements. Studies on solutions of vanadium (V) by e.m.f. techniques have indicated the decavanadate $[V_{10}O_{28}]^{-5}$ and $[H_2V_{10}O_{28}]^{-4}$ in the pH range 4 to 6. Studies by other experimental methods including measurement of the visible absorption spectrum,[1] ultracentrifugation,[2] and cryoscopic studies[3,4] have tended to confirm these results. E.m.f. studies have also indicated that the smaller polly-and mono-nuclear anions, $[V_3O_9]^{-3}$, $[HV_2O_7]^{-2}$, and $[HVO_4]^{-2}$, also exist in solutions in the pH range 8 to 10.[5]

Few solution studies have been carried out with the heavier V-B elements because their extremely basic nature makes such experiments difficult. Jander and Ertel[6] recently studied solutions containing niobium (V) using conductometric, u.v. spectrophotometric, and diffusion techniques. They reported that strongly alkaline solutions contained an anion $[Nb_6O_{19}]^{-8}$ and that this could be protonated to give $[HNb_6O_{19}]^{-7}$. On the other hand similar studies made on solutions of tantalum (V) led to the postulation of a pentatantalate.[7] These conclusions were drawn largely from measurements of diffusion coefficients and cryoscopic studies. Both of these experimental methods have been criticized.[8,9]

The polyanions of the Group V-B elements have been the subject of many investigations. Recently Schwarzenbach and Meier[10] found that both $HCrO_4$- and $[Cr_2O_7]^{-2}$ exist in acidified solutions of Cr(VI). Recent studies of Mo(VI) solutions using e.m.f. methods indicate that the polyanion $[Mo_7O_{24}]^{-6}$ plus the protonated species $[HMo_7O_{24}]^{-5}$ and $H_2Mo_7O_{24}]^{-4}$ exist in the pH range 3 to 6.[11] An early light scattering work[12] indicated large polyions existed in acidified molybdate solution, and a recent light scattering study[13] indicated that the ion contains seven molybdenum atoms. Very recently it was shown by equilibrium ultracentrifugation[14] and by raman spectroscopy that ions containing either seven or eight molybdenum atoms exist in acid aqueous solution. X-ray studies[15] show that these same species, $[Mo_7O_{24}]^{-6}$ and $[Mo_8O_{27}]^{-6}$ are present in the solid state.

Both e.m.f.[16] and ion exchange[17] studies indicate that anions containing six tungsten atoms and with net charges of minus 2 exist in acid aqueous solution. These are written most simply as protonated forms of $[HW_6O_{21}]^{-5}$.

Since the stereochemistry of tantalum in oxygen compounds is rather simple, it was decided to study alkaline tantalate solutions as a model system for the investigation of polyanion formation. The potassium tantalate, $K_8Ta_6O_{19}.16H_2O$, is extremely soluble in water and appeared suitable for study. X-ray work[18] on the crystals has shown that they contain hexatantalate anions of cubic symmetry.

II THE PROPOSED METHOD OF ATTACK

The essentially independent methods of e.m.f. measurements, light scattering, and equilibrium ultracentrifugation provide the necessary basic information to determine the charge and degree of polymerization of anions existing in alkaline aqueous solution. E.m.f. studies using a glass electrode make clear the concentration ranges where the polymerization reactions are rapid and reversible. Under favorable conditions the formulas of the polymers predominating in each region can be determined and stability constants calculated. Charge transfer bands in the ultraviolet should indicate the presence of any new species by a shift in the absorption region.

Finding regions where one isopolyion predominates is possible. Such monodisperse systems can be subjected to analysis by light scattering. Tobias and Tyree[19] have outlined the theory for such work and have successfully applied it to the hydrolyzed bismuth (III) system.[20]

With sufficiently stable solutions, equilibrium ultracentrifugation using methods developed by workers at Oak Ridge[21] should give a good check on the reliability of the light scattering results. Use of both schlieren[22] and interference-type[23] optics should provide an additional experimental check over a wide range of polyion concentrations.

Finally, it would seem reasonable to bind tantalates to an anion exchange resin,[24] and after measuring the equilibrium pH to determine maximum charge from thehydroxide ions displaced. Also if several species existed it might be possible to separate them by eluting with KOH solutions.

As a check on the precision and accuracy of light-scattering and ultra-centrifugation measurements, it was planned to use well-characterized potassium 12-tungstosilicate solutions as a model for a detailed study. The use of these solutions as "knowns" is justified since x-ray diffraction studies[25] on 0.3095 M $H_4SiW_{12}O_{40}$ solutions have confirmed that the single polyanion existing in these solutions is the same as that found in the crystals, i.e., $[SiW_{12}O_{40}]^{-4}$. Complementary light scattering[26] and ultracentrifuge[27] work has also been done.

III OUTLINE OF EXPERIMENTAL TECHNIQUES

E.m.f. Measurements

Methods for studying complex equilibria have been developed in great detail for systems involving both mononuclear[28,29] and polynuclear[30,31] species. Data are usually gathered and expressed in terms of an average ligand number $\bar{n}$ or z, equalling the average number of ligands bound per metal atom. For an unknown system containing the various species M_qX_p where B is the total concentration of metal, M; A is the total (analytical) ligand concentration, b is the equilibrium concentration of the free ligan, X^-; and K_{pq} is the equilibrium constant for formation of the species: given A, a and B to good precision all K_{pq}'s

can be calculated. If only mononuclear species MXp are present in solution, the ligand number n will be independent of B. Thus, if for such a system "a" represented the hydroxide ion concentration a plot of the ligand number vs. pH would be independent of B.

Such plots contribute information which can be used to find regions of monodispersity if such exist. This latter condition is most important in light scattering and equilibrium ultracentrifugation. Polydisperse systems at present seem too complex to be subject to successful analysis.

Light Scattering

Einstein[32] first suitably explained the turbidity of liquids as due to local thermal fluctuations in density. Solutions are more turbid than pure liq uids since local differences in concentration augment solvent thermal irregularities in the refractive index. Debye[33,34] reduced the turbidity equation to one containing easily measured quantities. Stockmayer[35] and independently Kirkwood and Goldberg,[36] developed a general equation for the fluctuations of the refractive index in multicomponent systems with no angular dissymmetry permitting the interpretation for such systems.

Tobias and Tyree[19] have developed the following modification of the equation of Stockmayer for solutions of low molecular weight polymeric electrolytes in the presence of high concentrations of supporting electrolytes.

$$\frac{1}{N_{Z'}} = \frac{H''\phi\,\psi'^2 m'}{\tau^*} - \frac{Z'^2 m'}{2m_3} \qquad (1)$$

The equation is written for a monomeric composent defined to be $K(_{1.34} - \nu)K_{\nu}TaO_{3.16} - \frac{(1.34 - \nu)}{2}KCl$. Thus, $N_{Z'}$ represents the degree of polymerization; ψ' is the molar refractive index increment of the component; m' is the componenet molarity; τ^* is total solution turbidity minus supporting electrolyte turbidity. $Z' = 1.34 - \nu$ where ν is the number of potassium ions bound per monomer component. ϕ is the volume fraction of the solvent; and m_3 is the concentration of the supporting electrolyte.

Essentially, equation 1 has two unknown quantities, $N_{Z'}$ and Z'. Theoretically, measurements of turbities of two solutions of different m' should suffice to solve for $N_{Z'}$ and Z'. In practice it is best to measure several solution turbidities over as wide a range of m' concentration as possible. Plotting $1/N_{Z'}$ as a function of Z' for each concentration of polymer in solution is perhaps a more accurate method of determining the experimental quatities. A family of smooth curves results which intersect at the best values of $1/N_{Z'}$ and Z'.

Ultracentrifugation

The general theory of sedimentation equilibrium has been outlined by Svedberg and Pedersen.[37] For a solution containing a sedimenting component i,

$$d\ln a_i = \frac{M_i(1-v_i Px)w^2 d(x^2)}{2RT} \qquad (2)$$

a_i = activity of component i, M_i = molecular weight, v_i = partial specific volume, P = density of solution, and w = angular velocity of the rotor. If the activity coefficient is constant a plot of ln m' vs. x^2 will allow one to calculate M_i for a nonelectrolyte. However, if the solute is ionized one must know the charge, Z', to solve for M_i.

For charged species the sedimentation equation becomes

$$N_{Z'} = \frac{S/A'}{1-\frac{(Z')^2 m'S}{2m_3 A'}} \quad (3) \qquad \text{where} \qquad A' = \frac{M'(1-v_i Px)w^2}{2RT} \quad (4)$$

Actually with schlieren optics what is measured is $S_e = d\ln(Z^*/x/d(x^2))$ where Z*, the displacement of the bar image, is proportional to the refractive index gradient at x. The relationship between S_e and S is as follows. $S_e - S = d\ln S/d(x^2)$. Calculation of $N_{Z'}$ and Z' therefore requires measuring S_e for solutions of varying solute concentration, calculating A' and S, and solving for N for assumed values of Z' for each of these solutions. The intersection of $N_{Z'}$ and Z' plots for the various solutions will indicate the best value for $N_{Z'}$ just as is done for the light scattering.

In the past five years interference optical systems have been described[23,27,38] which follow changes in concentration of solutes by measuring directly the difference in refractive index. A double compartment cell replaces the single compartment schlieren cell. One section holds the solvent, polymer, and supporting electrolyte, while the other contains an identical solution minus the polymeric solute. The paired cell compartments are sector shaped, the same size, and occupy positions during centrifugation identical to one another, but for rotation about the centrifuge axis. Monochromatic light passes by way of slits on the cell bottom through each compartment and produces interference fringes when recombined on the far side. From the positions of the fringes at equilibrium the distribution of the solute as a function of the distance from the center of rotation can be determined. Again $N_{Z'}$ and Z' are determined simultaneously using the results of two or more experiments run at varied solute concentrations.

IV EXPERIMENTAL RESULTS

Potential measurements were made using a lithium glass electrode and a calomel electrode system in 0.5 M KCl. The work showed that about 0.12 hydroxide ions appeared in solution for each tantalum atom dissolved as the tantalate salt. This amount did not vary much with pH to the point where hydrous Ta_2O_5 precipitated irreversibly around pH 11.

Aqueous potassium tantalate absorbed strongly in the u.v. below 2600 Å. At 2100 Å the extinction coefficient was $2.6 \cdot 10^4$ and apparently the peak was below 2000 Å since none was detected. No shift

in the band was observed as the total tantalum concentration and hydroxide concentration were varied. In the infrared region bands appeared for tantalate at 965, 910, 822, and 710 cm.$^{-1}$.

Potassium tantalate was successfully bound to Dowex 2-X4 anionic resin in the hydroxide form. From KOH displaced it was determined that the maximum charge per monomer unit was about 1.12 compared to the maximum possible 1.34.

Turbidity data showed that tantalate in 1 M KCl has a degree of polymerization of about six and an effective ionic charge of about -2. Depolarization measurements indicated a species of high symmetry. The tungstosilicate in 0.5 M KCl showed a degree of polymerization slightly greater than 1 and a charge of -2.

Schlieren centrifugation results agreed well with those of the light scattering. The precision was about the same and the values of $N_{Z'}$ and Z' were identical within experimental error. Interference data showed more scatter, but again did not disagree with the other data.

V CONCLUSIONS

E.m.f. measurements, u.v. spectra, and anion exchange chromatography have idicated that the tantalate anions in aqueous solution are probably of approximately the same stoichiometry as their crystalline counterparts. It seems very unlikely in the light of the e.m.f. data that any tantalate monomer such as $[TaO_4]^{-3}$ exists in the solutions studied, i.e., below pH 13, since $\bar{n}$ values remained constant and quite small as the pH varied. Even better evidence that tantalate solutions contained only one anionic species came from the schlieren and interference unltracentrifugations.

It is certain that the effective charge, Z', is lowered much more by the binding of potassium ions from the supporting electrolyte than by hydrolysis. What the precise magnitude of Z' really means is subject to some interpretation. Values of $N_{Z'}$ did agree within an experimental error of less than ten percent for both techniques. This study has shown that tantalate polyanions are of high symmetry and probably contain six metal atoms. It is very likely that the species present in solution is nearly identical to that found in the solid state. The effective charge on the hexatantalate is most likely between -2 and -3.

Use of solutions of the well-characterized, highly symmetrical 12-tungstosilicate anion as a "known" has provided a check on the validity of the approximations made in the theoretical treatment of light scattering and ultracentrifugation equations.

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COORDINATION CHEMISTRY OF SELENIUM

Monther Y. Aljanabi July 7, 1964

INTRODUCTION

The selenium atom can be regarded as a Lewis acid and as a Lewis base, because it is an electron acceptor in compounds such as H_2Se, D_2Se(1), SeSn(2), SCSe(3), etc., and it is an electron donor in compounds such as SeO_3(4), Se_2Cl_2, Se_2Br_2(5), $SeCl_4$(6), SeS_2, etc.

This seminar will consider the coordination chemistry of those compounds in which selenium is the central atom as well as those compounds in which selenium, in an anion, is a ligand.

COMPOUNDS IN WHICH SELENIUM IS THE CENTRAL ATOM

$SeCl_4$

Selenium, a third row element, would not be expected to show appreciable double bond character in the $SeCl_4$. One can obtain some estimate of the double bond character by using the procedure outlined by Mays and Dailey(7). Using the published data(8) for Se-Cl bond length in $SeCl_4$ and the single-bond and double-bond covalent radii for Se and Cl, Bray(6) found that $SeCl_4$ has approximately 21% ionic character, 73% single bond character and 6% double bond character. He also calculated the value of $1-|U_p|$, where U_p, the number of the unbalance p electrons on the halogen, is given by

$$|U_p| = |(eqQ)_{molecule}| \; /2 \; |(eqQ)_{atom}|$$

If the value of $1-|U_p|$, which is equal to 0.33 - 0.37 for $SeCl_4$, is plotted as a function of the electronegativity difference, 0.7(9) or 0.6(10) for $SeCl_4$ the point falls on the line joining the carbon, germanium, and tin tetrahalides but deviates toward the line which includes the silicon tetrahalides and which is different because of appreciable double-bond character in these compounds.

In this comparison of $SeCl_4$ with Group IV tetrahalides, it must be remembered that selenium differs from the elements of Group IV by lacking two p-shell electrons. Furthermore, published x-ray data indicate that the tetrahedral structure model is probably only approximate in $SeCl_4$ which has six resonances while carbon germanium, silicon, and titanium were found to have four to sixteen resonances.(12)(13)

$Se(CN)_2$ and $Se(SeCN)_2$

An x-ray structure determination by Hazell(14) shows that selenium cyanide is an orthorombic crystal which has unit cell dimensions a = 8.71, b = 6.98 and c = 13.41 A°. The V-shaped molecules lie in parallel planes, 3.35 A° apart, perpendicular to c axis. This layer structure accounts for ease of cleavage of the crystals. Bond lengths(15) (standard deviation 0.1 A°) are Se-C = 1.86 A° , C-N = 1.42 A° and the bond angles (standard deviation 6°) Se-C-N = 177°, C-Se-C = 119°. Aynstey, Greenwood, and Sprague(15) have reported the selenium cyanide stretching frequencies which are given in Table 1.

The selenium cyanide molecule has C_{2v} symmetry with eight infrared active and nine Raman active normal modes of vibration while selenium selenocyanate has C_s symmetry in the crystal lattice.(16) Seven of the fifteen modes were observed while the other modes could not be observed because of the low frequencies.

Table 1

Stretching Frequencies of Selenium Cyanide

Frequency $\nu(cm^{-1})$	Assignment			
2183				
2175		antisym.	C ≡ N	stretch
608		antisym.	C - Se	stretch
516		sym.	C - Se	stretch
436		sym.	Se - C_2	bending
346				
336	sym.	antisym.	Se -C ≡ N	bending
312	out of plane deformation			
302	?			

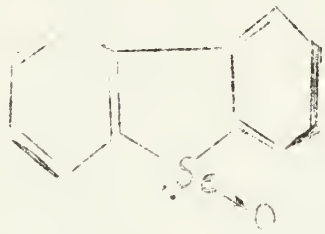
SeO_3^{2-}

Riley(17) has prepared selenitopentamminecobalt (III) selenite $[Co(NH_3)_5SeO_3]_2[SeO_3].3H_2O$ and $[Co(NH_3)_5SeO_3]Cl$ but his experiment did not show whether the selenite group is attached through selenium or oxygen.

COMPOUNDS IN WHICH SELENIUM IS A DONOR ATOM

Diarylseleno oxides

Gould and McCullough(18) have reported that diarylseleno oxides, such as dibenzoselenophene oxide (Figure 1)



(Figure 1)

coordinate to mercury (II) through the selenium atom in compounds $(p\text{-}CH_3OC_6H_4)_2SeO.HgCl_2$, $(p\text{-}C_2H_5OC_6H_4)_2SeO.HgCl_2$, and $(C_6H_4)_2SeO.HgCl_2$, but no evidence was presented to support their conclusion.

Selenocyanates (M-SeCN) and isoselenocyanates (M-NCSe)

The coordinating tendencies of the thiocyanate ion are well known, but relatively little is known about the selenocyanate ion. Selenocyanates have been found to be Se-bonded to metals of class (b) character(19), e.g., $K_2[Pt(SeCN)_6]$, $K_2[Hg(SeCN_4]$, and AgSeCN, and N-bonded to metals of class (a) character such as Co (II)(20)(21) and Cr(III),(22) e.g. $[CH_3)_4N]_2[Co(NCSe)_4]$ and $K_3[Co(NCSe)_6]$. The third type of bonding of the selenocyanate ion, as a bridging group has been reported for $HgCo(NCSe)_4$(20)(21)

It has been found, from x-ray structural determination, that the two mercury compounds $HgCo(NCSe)_4$ and $HgCo(NCS)_4$ are isomorphous.(20)(21)(23) Turco et al., (21) have made the assumption that the nature of the coordination in selenocyanates must be similar to that of the corresponding thiocyanates.

The thiocyanate ion $:N \equiv C - \ddot{S}:^-$ is known to form both thiocyanato (M-SCN) and isothiocyanato (M-NCS) complexes depending on the central metal atom employed.(24) Recently, Pearson(25) has suggested that sulfur in the SCN^- ion is "soft" and tends to coordinate with a metal of class (b) (polarizable metal) character, whereas nitrogen in the SCN^- ion is "hard" and prefers to coordinate to a metal of class (a) (nonpolarizable metal) character.

Burmeister and Basolo(26) have reported the effects of a series of ligands on thiocyanate bonding in palladium (II) and platinum (II) complexes and the synthesis,(27) characterization and preliminary kinetics of the isomerization of thiocyanato and isothiocyanato isomers of some palladium (II) complexes. It is known that NCS^- does not depend on the metal

only to form N-bonded or S-bonded complexes but also depends on electronic and steric factors.(26)(28)

The C - N stretching frequencies of the selenocyanato complexes increase in the order M - NCSe $\ll$ $NCSe^-$ $<$ M - SeCN $<$ M - SeCN - M, which is different from the order observed for thiocyanates, namely, NCS^- $<$ M - NCS $<$ M - SCN $<$ M - SCN - M.(29) The C - Se stretching frequencies shift, relatively to uncoordinated $NCSe^-$, to higher frequencies upon nitrogen coordination and to lower frequencies upon selenium coordination which is completely analogous to the behavior of the thiocyanates. Turco *et al.*,(21) have reported that the C - N stretching frequencies of $NCSe^-$ appeared to be less than 2080 cm^{-1} for M - NCSe and greater than 2080 cm^{-1} for M - SeCN while the C - Se stretching frequencies were around 650 cm^{-1} (700-600 cm^{-1}) for M - NCSe and around 550 cm^{-1} (500-600 cm^{-1}) for M - SeCN. Stretching frequencies of C - N, C - Se, and C - S for different compounds are collected in table II.

Attempts have been made by Burmeister and Al-Janabi(30) to prepare new compounds of cobalt (III) and platinum (II) with the NCSe and NCS^- ions, but the results have not yet been published. Several new compounds, e.g., $Pt(bipy)(SeCN)_2$, $Pt(phen)(SeCN)_2$, $[Co(NH_3)_5NCSe](NO_3)_2$, $K_3[Co(CN)_5NCSe]$, and $K_4[(CN)_4Co\begin{smallmatrix}\nearrow NCS \\ \searrow SCN\end{smallmatrix}Co(CN)_4] \cdot 4H_2O$ have been reported. The C - N and C - Se stretching frequencies of these compounds are shown in Table III.

Table II

The C-N, C-S, and C-Se Stretching Frequencies in Some Inorganic Thiocyanate and Selenocyanate Compounds (cm^{-1})

Compounds	ν_3C-N	ν_1C-S	ν_1C-Se	Ref.
KSCN	2053 s	748 w		31
KSeCN	2070 s		558 w	32
$K_2[Hg(SCN)_4]$	2115 s	716 w		21
$K_2[Hg(SeCN)_4]$	2098 s		543 w	21
$K_2[Pt(SCN)_6]$	2125 s	694 w		33
$K_2[Pt(SeCN)_6]$	2124 s		520 w	21
$[(CH_3)_4N]_2[Co(NCS)_4]$	2075 s			20
$[(CH_3)_4N]_2[Co(NCSe)_4]$	2075 s			20
$[(C_2H_5)_4]_2[Co(NCS)_4]$	2053 s	840		21
$[(C_2H_5)_4N]_2[Co(NCSe)_4]$	2053 s		672 m	21
$K_3[Cr(NCS)_6] \cdot 4H_2O$	2105 s	820		34
$(NH_4)[Cr(NH_3)_2(NCS)_4]$	2110 s			22
	2042 sh			
$[(CH_3)_4N]_3[Cr(NCS)_6]$	2075 s			22
	2042 sh			
$[(CH_3)_4N]_3[Cr(NCSe)_6]$	2067 s			22
	2041 sh			
$[Co(quinoline)_2(NCS)_2]$	2062, 2045			20
$[Co(quinoline)_2(NCSe)_2]$	2070, 2037			20
$[Co(Ph_3PO)_2(NCS)_2]$	2070			20
$[Co(Ph_3PO)_2(NCSe)_2]$	2066			20
$[Co(py)_4(NCS)_2]$	2072			20
$[Co(py)_4(NCSe)_2]$	2073			20
$[Co(PPh_3)_2(NCS)_2]$	2040			20
$[Co(PPh_3)_2(NCSe)_2]$	2165,2137			20
	~ 2070 sh			
$[Pd(bipy)(SCN)_2]$	2117(m,sp)	700 w		26
	2108(s,sp)			
$[Pd(bipy)(SeCN)_2]$	2116 s		522.5 w	35
	2112 s		517.5 w	

Table III

The C-N and C-Se Stretching Frequencies in Some of the New Inorganic Thiocyanate and Selenocyanate Compounds (cm^{-1})

Compound	ν_3C-N(cm^{-1})	ν_1C-Se(cm^{-1})
$[Pt(bipy)(SeCN)_2]$	2130 s,sp	532 w
	2137 sh	526.5 w
$[Pt(phen)SeCN)_2]$	2123,2131 m	550 w
$[Co(NH_3)_5NCSe](NO_3)_2$	2070 s,sh	623.5 m
	2116 vvs	
$K_3[Co(CN)_5NCSe]$	2070 s	664
	2095 w	
	2124, 2127 vvs	
$K_4[(CN)_4Co\langle^{NCS}_{SCN}\rangle Co(CN)_4] \cdot 4H_2O$	2120 vvs	
	2180 s,m	

CONCLUSION

Although the published results indicate a close similarity in the coordination behavior of the thiocyanate and selenocyanate ions, the most recent work(30) has led to discovery of distinct differences between the two. For example, $[Pd(bipy)(SCN)_2]$ readily isomerizes to $[Pd(bipy)(NCS)_2]$ whereas $[Pd(bipy)(SeCN)_2]$ is stable with respect to isomerization. $K_2[Hg(SCN)_4]$ reacts with $[Co(CN)_5]^{3-}$ to form $K_4[(CN)_4Co\langle^{NCS}_{SCN}\rangle Co(CN)_4]$, whereas, under the same conditions, $K_2[Hg(SeCN)_4]$ reacts with $[Co(CN)_5]^{3-}$ to form $K_3[Co(CN)_5NCSe]$. No example has yet been found of a coordination complex wherein the normal bonding mode of the selenocyanate ion is changed by the presence of other ligands in the coordination sphere, nor has a steric effect been demonstrated.

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STRUCTURE OF METAL ALKOXIDES

Mark Wicholas July 14, 1964

INTRODUCTION:

Although metal alkoxides have been known for over a century, it is only in the last ten years that the determination of their structures has been attempted (1). On the basis of chemical and physical properties, there are three distinct groups of metal alkoxides: ionic, giant polymeric, and telemeric. One would intuitively expect the alkoxides of the alkali and alkaline-earth metals to be ionic (2), whereas one would expect those alkoxides which are giant covalent polymers to be the alkoxides of divalent-transition metals, of which all are completely insoluble in organic solvents (3). At present, very little is known of these alkoxides. The third group contains the monomeric and polymeric alkoxides, of which the degree of polymerization is found to vary from two to eight. In Table I, some representative alkoxides are listed together with their respective degrees of polymerization. Most research to date has involved these latter mentioned alkoxides. Bradley has sought to determine the complexity of these alkoxides in solution by applying both cryoscopic and ebulliometric techniques and controlled hydrolysis experiments. During the past three years, x-ray and N.M.R. studies have been made.

TABLE I

Some Representative Alkoxides and their Degree of Polymerization

Compound	n	Solvent	Reference
$TlOCH_3$	4.0	C_6H_6	4
$TlOC(CH_3)_2CH_2CH_3$	4.0	"	5
$Al(OC_2H_5)_3$	4.1	"	6 *
$Al(O^tBu)_3$	1.95	"	6
$Fe(OC_2H_5)_3$	2.9	"	7
$Fe(O^tBu)_3$	1.5	"	7
$Ti(OC_2H_5)_4$	3.0	"	8 *
$Ti(O^tBu)_4$	1.0	"	8
$V(OCH_3)_4$	2.79	"	9
$V(OC_2H_5)_4$	2.04	"	9
$Zr(OC_2H_5)_4$	2.24	"	10 *
$Zr(O^tBu)_4$	1.0	"	11
$Ta(OC_2H_5)_5$	1.98	"	12
$Ta(O^tBu)_5$	1.01	"	12
$Nb(OC_2H_5)_5$	2.02	"	13
$Nb(OCHCH_3C_2H_5)_5$	1.14	"	13
$U(OC_2H_5)_6$	1.2	"	14
$U(O^tBu)_6$	1.0	"	14

* Concentration Dependent.

Results of Cryoscopic, Ebulliometric and Hydrolysis Experiments.

The classical methods for determining the structure of alkoxides are ebulliometry, cryoscopy and controlled hydrolysis experiments. These have been used extensively by Bradley since 1952. Essentially, he has determined the degree of polymerization through cryoscopy and ebulliometry and has assumed that this number--if an integer--corresponds to the number of units per molecule in solution and also in the solid state. From the hydrolysis experiments, in which the complexity is measured as a function of the water added, Bradley (15) has developed a theory which predicts the structure of these alkoxides.

As an example, the hydrolysis experiments with titanium tetraethoxide (16), which has a degree of polymerization of 3.0 in benzene and 2.91 in ethanol, will be presented. When $Ti(OC_2H_5)_4$ was hydrolyzed, two different oxide-alkoxide polymers, $Ti_6O_4(OC_2H_5)_{16}$ and $Ti_9O_8(OC_2H_5)_{20}$, were isolated at different water/titanium ratios. Assuming that $Ti(OC_2H_5)_4$ is trimeric in solution, the following equations can be written.

$$(x+1)[Ti(OC_2H_5)_4]_3 + 4xH_2O = [Ti_{3(x+1)}O_{4x}(OC_2H_5)_{4(x+3)} + 8xH_2O$$

This reaction was studied ebulliometrically, and the observed degree of polymerization, n_{obs} was then compared with the value, n, based on the above model.

If h = mole ratio of H_2O/T_1

$h = 4x/3(x+1)$

$n = 3(x+1) = 12/4-3h$

A plot of n and n_{obs} vs h is shown in Figure 1, and good agreement was found when $h < 1.0$. In 1957, Bradley (17) refined this treatment by allowing for the presence of the solvated dimer $Ti_2(OC_2H_5)_8 \cdot 2C_2H_5OH$, since in ethanol $n_{oBS} = 2.91$ for pure $Ti(OC_2H_5)_4$. The curve for the system $[Ti(OC_2H_5)_4]_3 + Ti_2(OC_2H_5)_8 \cdot 2C_2H_5OH$ is also plotted on Figure 1 and presents better agreement with the observed data. Because of this agreement, Bradley concluded that $Ti(OC_2H_5)_4$ is trimeric in solution and titanium is in an octahedral environment. This work, however, has been criticized by Martin and Winters who claim that $Ti(OC_2H_5)_4$ is a cyclic trimer (18,19). Similar experiments with zirconium alkoxides (10) show that this hydrolysis data can be explained by assuming that these alkoxides are trimeric and have octahedrally coordinated zirconium atoms, and that tantalum alkoxides (20) are dimeric having octahedrally coordinated tantalum atoms.

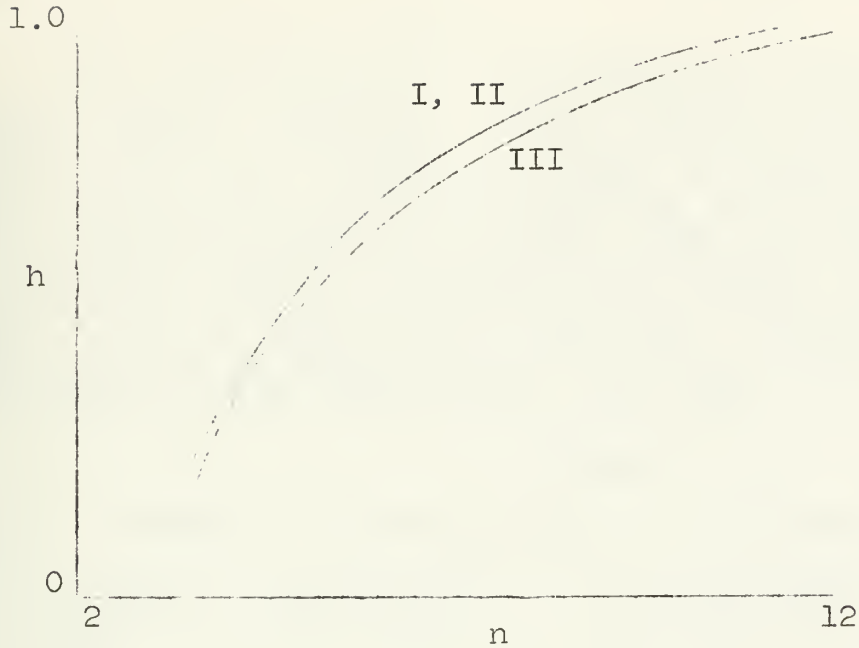

Figure 1.

Plots of the water/titanium mole ratio vs. the degree of polymerization for $Ti(OC_2H_5)_4$: I, observed curve; II, calculated curve based on the presence of $[Ti(OC_2H_5)_4]_3$ and $Ti_2(OCH_2H_5)_8 \cdot 2C_2H_5OH$; III, calculated curve based on the presence of $[Ti(OC_2H_5)_4]_3$.

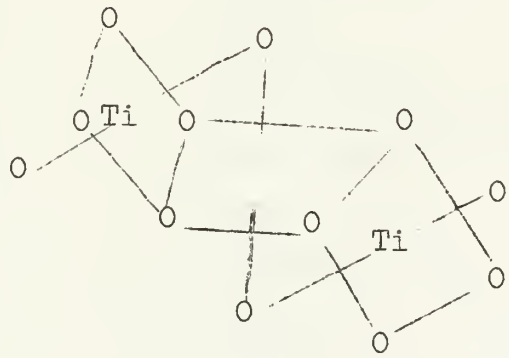

Figure 2.

Structure of $Ti(OC_2H_5)_4$ proposed by Bradley.

O = oxygen in OC_2H_5.

Structural Theory of Bradley

As a rationalization of the results of the hydrolysis experiments with $Ti(OC_2H_5)_4$ and of the observed degrees of polymerization found for the various alkoxides, Bradley advanced the following theory (15). Assuming that the coordination number of oxygen does not exceed four, and that the metal alkoxide adopts the smallest possible structural unit consistent with all the metal atoms attaining a higher coordination number through intermolecular bonding, then the stereochemistry of the metal atom can be predicted if the degree of polymerization is knwon. This is represented in Table II. Only for the aluminum alkoxides does he encounter difficulty in correlating this theory with the cryoscopic and ebulliometric data (21).

TABLE II

Degree of Polymerization as a Function of Stereochemistry

Compound	Coordination No. of M	Stereochemistry of M	Minimum Degree of Polymerization
MOR	2	OMO = 90°	2
	2	OMO = 120°	3
	3	pyramidal	4 *
$M(OR)_2$	3	planar-one OMO=90°	2
	3	planar OMO = 90°	3
	4	tetrahedral	3
	4	planar	4
	6	octahedral	∞
$M(OR)_3$	4	tetrahedral	2 *
	4	planar	2
	6	octahedral	8 *
$M(OR)_4$	5	trigonal bipyramidal	2
	6	octahedral	3 *
	8	cubic	8
$M(OR)_5$	6	octahedral	2 *
	8	cubic	4
$M(OR)_6$	8	cubic	2 *

* Prediction of Theory

X-Ray Determination of Structures

Complete x-ray structure determinations would naturally be most desirable for elucidating the structure of these polymeric alkoxides; however, the structures of only four alkoxides have been determined by this method. The crystal structure of thallous methoxide (22), which was known to be tetrameric in benzene (4), was found to be a tetramer in the solid state. Ibers (23) determined the crystal structure of titanium tetraethoxide and has found it also to be tetrameric, whereas in benzene solution it is trimeric. Wheatley (2,24) has determined the structure of lithium methoxide, and, as expected, this compound is ionic having the same structure, a layer type, as lithium hydroxide (25). In $LiOCH_3$, the Li-O bond distance is 1.95 Å as compared with a similar distance, 1.96 Å, in LiOH. It is worthwhile to mention briefly the crystal structure of the related mercury(II) methylmercaptide, $Hg(SCH_3)_2$ (26). Each mercury atom is covalently bonded to two sulfur atoms at a distance of 2.36 Å and weakly bonded to three other sulfur atoms at a distance of 3.25 Å. The intermolecular bonding through the mercaptide sulfur atoms causes a large polymeric molecule in which each mercury atom has an irregular tetragonal pyramidal environment.

A different technique, N.M.R., has been applied to this problem only in the related silyloxide system (27). The trimethylsilyloxides of aluminum and gallium, which have degrees of polymerization of two in benzene, have proton spectra containing two bands, thus corresponding to a dimeric structure with bridging silyloxide groups. The trimethylsilyloxide of boron, which is monomeric in benzene, has a proton spectrum containing only one band.

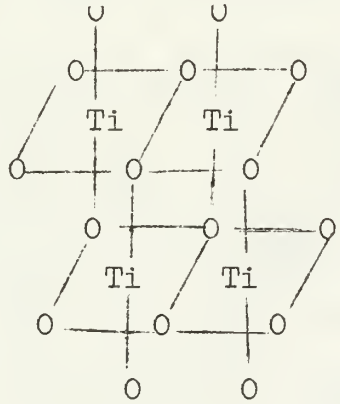

Figure 3.

Crystal Structure of $Ti(OC_2H_5)_4$

O = oxygen in OC_2H_5

Conclusion

The structural data presented has been of two types. From the cryoscopy, ebulliometry and hydrolysis experiments degrees of polymerization have been determined and the structures of various alkoxides have been inferred. The structural theory of Bradley is based solely on this type of data. The second type which is x-ray data, presents direct structural evidence and can be used to evaluate Bradley's theory.

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THE ELECTRONIC STRUCTURES OF COPPER(II) ACETATE and RELATED COMPOUNDS

Michael F. Rettig July 21, 1964

INTRODUCTION

Copper(II) ion, which has a d^9 electronic configuration, usually shows a room temperature magnetic moment in the range 1.9-2.2 B.M., corresponding to one unpaired electron with appreciable contribution from spin-orbit coupling. However, in 1915, Lifschitz and Rosenbohm(1) observed that the room temperature moment of copper(II) acetate monohydrate is anomalously low, being about 1.4 B.M. Since that time, much experimental and theoretical work has been done on $[Cu(CH_3CO_2)_2OH_2]_2$ and related compounds.(2) The general picture which emerges is that in certain instances two copper(II) ions are held together by four bridging groups, forming a binuclear complex. This circumstance gives short copper-copper distances, and "metal-metal" interaction. Several groups of theoretical chemists have attempted to elucidate the mechanism of this "metal-metal" interaction. One thing seems clear and should be stated at the outset: the "metal-metal" interaction in binuclear copper(II) compounds is weak, and it is not expected that a dimer would form on the basis of this interaction alone. Rather, it seems more reasonable to consider the "metal-metal" interaction to be a result, not a cause, of dimerization.

The purpose of this seminar is threefold: 1) the experimental data pertinent to a discussion of the electronic structure of $[Cu(CH_3CO_2)_2OH_2]_2$ will be reviewed; 2) several approximate treatments of the bonding in $[Cu(CH_3CO_2)_2OH_2]_2$ will be outlined and discussed in the light of the experimental data; and 3) some binuclear compounds related to $[Cu(CH_3CO_2)_2OH_2]_2$ will be briefly described.

EXPERIMENTAL RESULTS

<u>Magnetic Susceptibility Studies</u>: Table I summarizes the important magnetic results for solid samples.

Table I

Magnetic Behavior of Some Solid Copper(II) Alkanoates

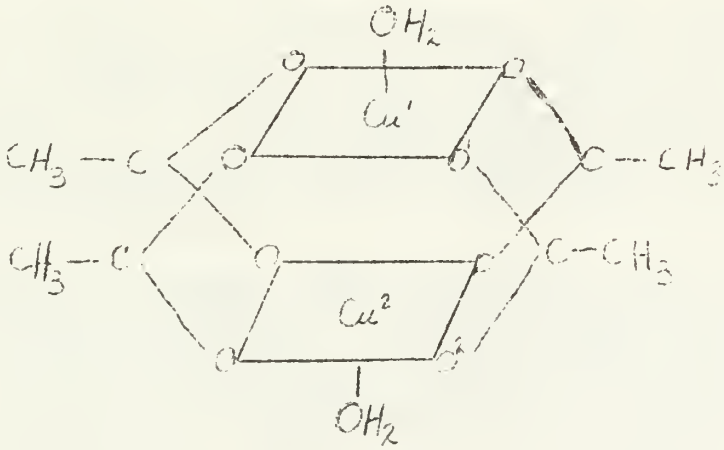
Compound	Temp.(K)	T_c(K) - J(cm^{-1})	g	(B.M.)[a]	Ref
$[Cu(CH_3CO_2)_2]_2$	90°-400°	270°	302	2.17	1.39	4
$[Cu(CH_3CO_2)_2OH_2]_2$	90°-400°	255°	286	2.13	1.41	3,4
$[Cu(RCO_2)_2]_2$ and $[Cu(RCO_2)_2OH_2]_2$ [b]	90°-400°	278°±28°	309±31	2.15±.08	1.35-1.41	5
$[Cu(HCO_2)_2L_n]_2$ [c]	85°-370°	500°	550	2.16	0.96-1.10	7
$[Cu(CH_3CO_2)_2L]_2$ [d]	94°-350°	298°±9°	329±8	2.27±.05	1.34-1.40	8
$[Cu(C_3H_7CO_2)_2L]_2$ [d]	94°-350°	300°±5°	333±9	2.21±.03	1.32-1.37	8
$[Cu(C_3H_7CO_2)_2L']_2$ [e]	94°-350°	97°±6°	112±12	2.18±.00	1.73-1.76	8
$[Cu(ClCH_2CO_2)_2(OH_2)_n]_2$ and $[Cu(Cl_2CHCO_2)_2(OH_2)_n]_2$ [f]	-----	----	--	---	1.42-1.74	10
$[Cu(Cl_3CO_2)_2]_x$ [g]	-----	----	--	---	1.77	10
$[Cu(Cl_3CO_2)_2OH_2]_x \cdot 2H_2O$ [g]	------	----	--	---	1.89	10

[a] measured at room temperature; [b] R is propionate, butyrate, laurate, stearate, or behenate. Results are stated as mean ± mean deviation of results for all compounds in the series; [c] n = 1 for pyridine, α-, β-, γ-picoline, and n = 1/2 for dioxane; [d] L is nothing, water, pyridine, α-, β-, or γ-picoline; [e] L' is aniline, p- or m- toluidine; [f] n is zero or 4, result is range of observed values; [g] may or may not be binuclear (x unknown)

It was found that the magnetic moments of the copper(II) alkanoates in benzene or dioxane solution are nearly the same as those of the solids.(6) Kondo and Kubo(9) determined the room temperature magnetic moment of copper(II) acetate in various solvents. The results are as follows: methanol (1.58 B.M.); ethanol (1.43 B.M.); dioxane (1.37 B.M.). These moments are subnormal, and it was concluded that the binuclear structure persists in methanol, ethanol, and dioxane.

Electron Spin Resonance: Bleaney and Bowers(11) determined the ESR parameters for single crystals of $[Cu(CH_3CO_2)_2OH_2]_2$. It was found that the "paramagnetic units" in the unit cell behave as would a species of spin S = 1. In other words, pairs of copper(II) ions are so situated in the unit cell that the unpaired spins of each copper(II) ion are strongly coupled. The intensity of the resonance lines decreased with a decrease in temperature and, at 20°K, no spectrum was observed. This was interpreted to mean that the triplet state is less stable than the singlet, and only through thermal excitation is the triplet occupied above 20°K. Bleaney and Bowers obtained $g_{\perp} = 2.08 \pm .03$ and $g_{\parallel} = 2.42 \pm .03$ at 90°K. Later Abe and Shimada(12) reported $g_x = 2.05$, $g_y = 2.09$ and $g_z = 2.34$ for $[Cu(CH_3CO_2)_2OH_2]_2$ at 300°K.

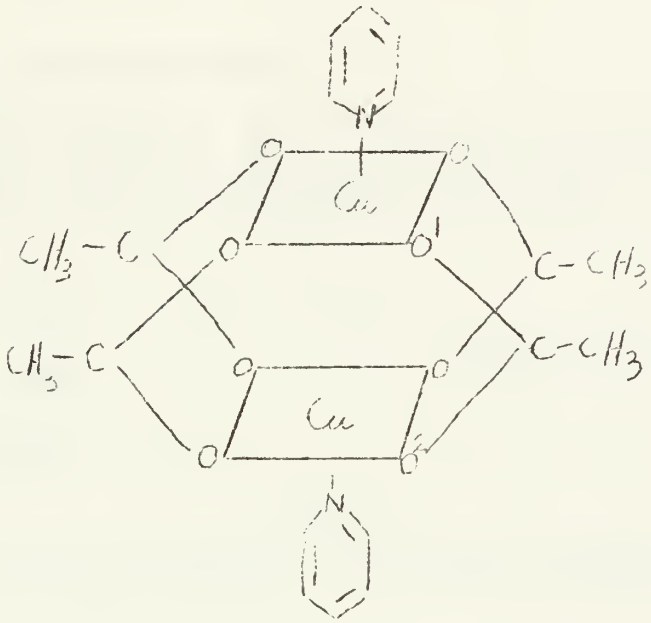
X-Ray Structure Determinations: An x-ray structure determination has been done for $[Cu(CH_3CO_2)_2 \cdot OH_2]_2$.(13) The main features of the structure are shown in Figure 1. Note the short copper-copper distance and that the four oxygen atoms lie 0.22 A° below the plane of the copper(II) ion. It was considered that the short copper-copper distance must lead to a "metal-metal" bond, but the authors did not elaborate.(13)



$Cu-OH_2$(2.20 A°); C-O(1.33 A°); Cu-Cu(2.64 A°); O^1-O^2(2.20 A°); $Cu-O^1$(1.97 A); $\angle O^1-C-O^2$(112°); $\angle O^1-Cu^1-Cu^2$(83°).

Figure 1

The crystal structure of $[Cu(CH_3CO_2)_2C_5H_5N]_2$ has been determined.(14) This structure is shown in Figure 2.



$Cu-O^1$(1.98 A°); $Cu-N$(2.12 A°); C^1-O^2(1.24 A°); $Cu-Cu$(2.63 A°); O^1-O^2(2.20 A°); $\measuredangle$ O^1-C-O^2(125°). The angle between the planes of the pyridine rings is 60°.

Figure 2

The structure of a second crystal modification of $[Cu(CH_3CO_2)_2C_5H_5N]_2$ has also been reported.(15,48) There are two important differences between this structure and that shown in Figure 2: 1) the copper-copper distance is 2.70 A°; 2) the pyridine rings lie in the same plane. A rationalization of these differences has not been advanced, but the effects may arise from pi-bonding.

<u>Absorption Spectra</u>: Both polarized single crystal and solution spectra are available for copper(II) acetate and certain of its derivatives. Compounds having the binuclear structure absorb in the range 7000-7500 A° (13,300-14,300 cm^{-1}) and have another band (considered to be diagnostic of copper-copper interaction) at 3750 A° (ca. 27,000 cm^{-1}). The former band is x,y polarized while the latter is z polarized.(16,17) Low temperature polarized spectra for $[Cu(CH_3CO_2)_2OH_2]_2$ have been determined.(19) Solution spectra for compounds of the type $[Cu(RCO_2)_2L]_2$ show an insensitivity to the nature of the R group(20,21), while variations of L lead to more pronounced shifts.(21,8) Graddon(22,23,46) concluded that the copper(II) acetate spectrum is typical of penta-coordinate copper(II),

and that the 3750 A° band is not necessarily diagnostic of metal-metal interaction.

THEORETICAL INTERPRETATIONS

$[Cu(CH_3CO_2)_2OH_2]_2$ was discussed qualitatively by Figgis and Martin in 1956.(4) These authors based their argument on the energy level scheme given by Polder,(25) shown in Figure 3. The bonding interaction was postulated to arise

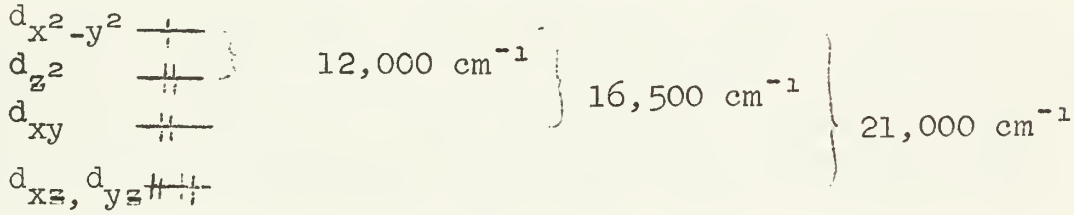
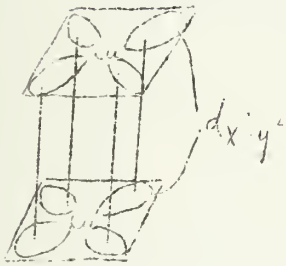


Figure 3

from $d_{x^2-y^2}$ -$d_{x^2-y^2}$ overlap, as shown in Figures 4 and 5.



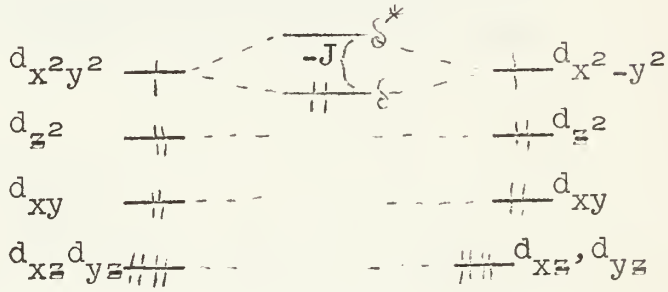


Figure 4 Figure 5

As indicated in Figure 5, the bonding electrons occupy an orbital of δ symmetry, and the bond is described as a "delta-bond." The authors considered that the two highest energy levels are δ and δ^*, and they did not specify the interactions among remaining d-orbitals. In this model, the energy difference between the states $(\delta)^2(\delta^*)^0$ and $(\delta)^1(\delta^*)^1$ corresponds to the experimentally determined singlet-triplet splitting, -J. A σ-bonded model, where the highest unoccupied level is derived from d_{z^2} d_{z^2} interaction, was rejected as being energetically unfavorable.

In 1959, Ross(26) gave a more detailed account of the bonding in $[Cu(CH_3CO_2)_2OH_2]_2$. Using valence bond and crystal field theory, he obtained the scheme shown in Figure 6. This

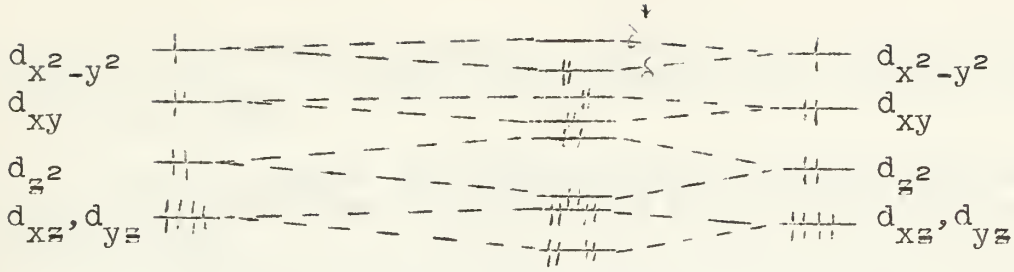


Figure 6

more detailed treatment agreed with the earlier description in terms of a "delta-bond".(4) Ross rejected a possible alternative description in terms of σ-bonding by comparing predicted and observed g-values. Ross and Yates(27) showed that the singlet-triplet splitting calculated for the "delta-bonded" model could be brought into agreement with the experimental value of -J.

In 1962, Forster and Ballhausen(18) discussed $[Cu(CH_3CO_2)_2OH_2]_2$ from an LCAO-MO viewpoint. These investigators used the Stark splitting pattern derived previously by Holmes and McClure(28) for copper(II) ion (Figure 7) in order to obtain their LCAO-MO Scheme (Figure 8). The empty

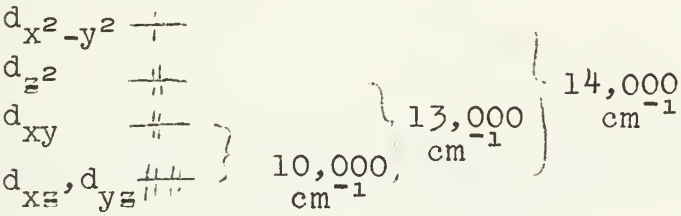


Figure 7

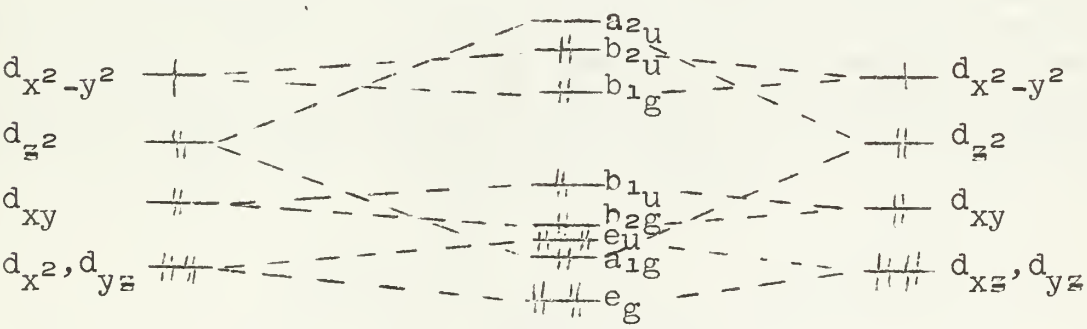


Figure 8
(not drawn to scale)

a_{2u} molecular orbital implies that any net stabilization arises from a d_{z^2}-d_{z^2} σ-bond, in contrast to the earlier described δ-bond.(4,26)

Tonnet, Yamada, and Ross(19) have compared the valence bond and LCAO-MO descriptions, and have reaffirmed the δ-bonded model.

Boudreaux(29) gave a second molecular orbital description of $[Cu(CH_3CO_2)_2OH_2]_2$, using what he felt was a more realistic Stark splitting for the d-levels. This scheme is shown in Figure 9. Boudreaux' results indicate a σ-bond, as did

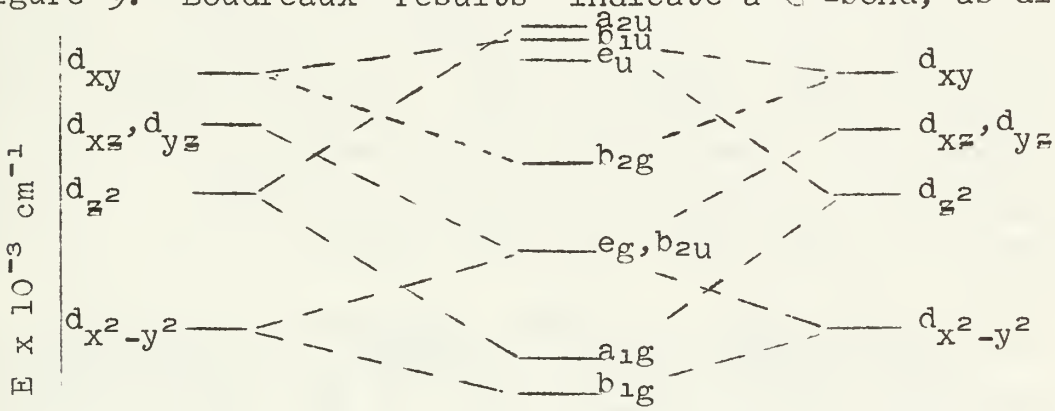


Figure 9

the earlier MO description.(18) Further, this scheme was found to be consistent with several experimental parameters, as will bediscussed in seminar.

Magnetic coupling by Kramers' superexchange mechanism (30,49-54) has received little attention in connection with the present problem. This mechanism involves spin coupling of magnetic ions through the agency of intervening non-magnetic groups. Superexchange apparently operates in antiferromagnetic $Cu(HCO_2)_2 \cdot 4H_2O$(31, Figure 10) It has been generally felt that the short copper-copper distance in the binuclear

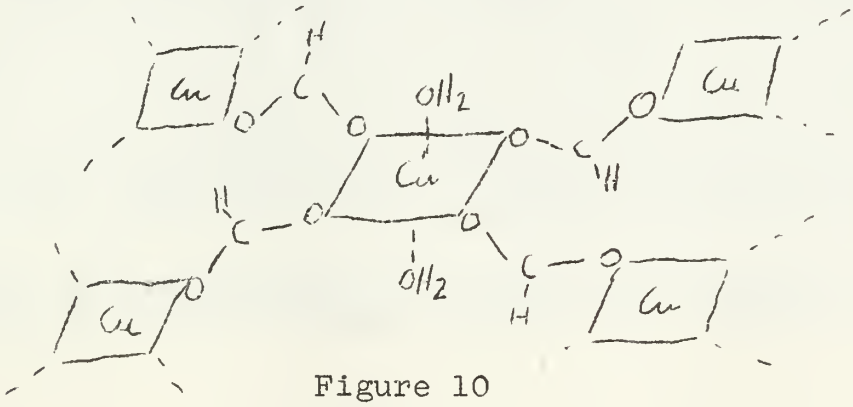


Figure 10

compounds favors the direct mechanism, but the superexchange mechanism, it would appear, has not been ruled out either theoretically or experimentally.

RELATED SYSTEMS

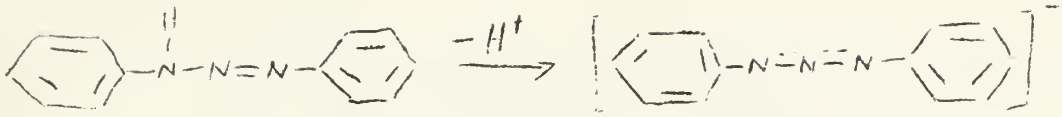
Rhodium (II) Carboxylates: The structure of diamagnetic(24) $[Rh(CH_3CO_2)_2OH_2]_2$ has been determined by x-ray methods.(33) This compound is isostructural with $[Cu(CH_3CO_2)_2OH_2]_2$, the rhodium-rhodium distance being 2.45 A°. The magnetic behavior is clearly anomalous, since rhodium(II) is a d^7 ion, and should be paramagnetic. Anhydrous $[Rh(CH_3CO_2)_2]_2$ as well as adducts with the following ligands have been prepared(34): H_2O, tetrahydrofuran, CH_3CN, dimethylsulfoxide, $(CH_3)_2S$, $(CH_3)_3N$, CH_3COOH, pyridine, NH_3, NO, ethylenediamine and o-phenanthroline. Infrared spectra were used to infer that the anhydrous acetate and adducts are binuclear. Absorption spectra and extinction coefficients were reported for this series, but there seems to be no magnetic data.(34) Also, $[Rh(CF_3CO_2)_2]_2$ and some adducts were prepared.(34)

Chromium (II) Acetate: Anhydrous chromium(II) acetate and the monohydrate are diamagnetic at room temperature.(35) $[Cr(CH_3CO_2)_2OH_2]_2$ was found to be isostructural with $[Cu(CH_3CO_2)_2OH_2]_2$.(36,37) The chromium-chromium distance is 2.64 A°, and this was taken as evidence for "direct interaction" of the metal ions. Chromium(II) is a d^4 ion, and it is possible that the electrons are paired in single ion orbitals. Of course it is also possible that the spins are paired in molecular orbitals. Furlani(38) has discussed $[Cr(CH_3CO_2)_2OH_2]_2$ from the electrostatic crystal field viewpoint.

Other Carboxylates: Molybdenum(II) and rhenium(III), both d^4 ions, were found to form diamagnetic carboxylates.(39,40) It was shown(40) that the rhenium(III) species are dimeric in solution, having the formula $[Re(RCO_2)_2Cl]_2$, and the workers pointed out that "it is not necessary to invoke metal-metal bonding to account for the diamagnetism."(cf. above)

Bridging Atoms Other Than Oxygen: Nortia(41) observed that red cupric thioacetate is diamagnetic at room temperature, with absorption bands at 3750 A° (28,000 cm^{-1}) and 5400 A° (18,000 cm^{-1}). These bands were compared to the bands in $[Cu(CH_3CO_2)_2OH_2]_2$, which appear at 28,000 cm^{-1} and 14,000 cm^{-1} in the reflectance spectrum. It was suggested(41) that the shift to 18,000 cm^{-1} in the thioacetate arises from increased tetragonality in the crystal field. Nyholm(42) gave a tentative rationalization of the magnetic differences in the thioacetate and the acetate.

A very interesting series of complexes is formed by deprotonated 1,3-diphenyltriazene (Figure 11). Harris and Martin(43)



1,3 diphenyltriazene (Tr-H) 1,3 diphenyltriazenide (Tr^-)

Figure 11

obtained the dark green $[CuTr_2]_2$. This compound is diamagnetic in the solid state from 80°K - 400°K., and is dimeric and diamagnetic in benzene solution. $[CuTr_2]_2$ shows a broad absorption band centered at about 6250 A°. Figure 12 shows the structure of $[CuTr_2]_2$, assigned on the basis of the foregoing evidence.

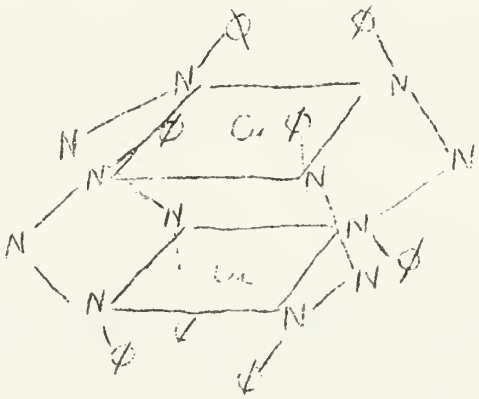
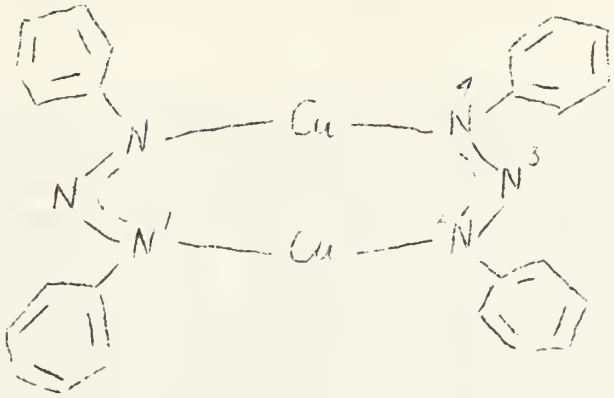


Figure 12

The anomalous magnetic behavior of $[CuTr_2]_2$ was considered to arise from direct metal-metal interaction.(43) It will be observed that the spin pairing here is stronger than in the copper(II) alkanoates. The investigators considered(44) that the dimeric, diamagnetic compounds $[NiTr_2]_2$ and $[PdTr_2]_2$ are isostructural with $[CuTr_2]_2$. $[Co(II)\ Tr_2]_2$ has been reported to have a magnetic moment of 2.1 B.M. at room temperature.(45) The electronic spectra of $[CuTr_2]_2$, $[NiTr_2]_2$, and $[CoTr_2]_2$ were recorded.(45) Graddon(46) mathematically resolved the visible peak of $[CuTr_2]_2$ into Gaussian components at 15,000 cm^{-1} and 19,000 cm^{-1} (a band near 27,000 cm^{-1} is obscured by charge transfer absorption). He concluded that $[CuTr_2]_2$ shows a typical tetracoordinate copper(II) spectrum. It appears that no crystal structures have been determined for compounds of the type $[M(II)Tr_2]_2$. However, the structure of $[Cu(I)Tr]_2$ has been determined by x-ray methods,(47) and is shown in Figure 13.



$\measuredangle$ N^1-Cu-N^2(172°);

Cu-Cu(2.45 A°); N^2-N^3(1.316 A°); N^3-N^4(1.274 A°); Cu-N^4(1.92 A°)

Figure 13

With small deviations, all the atoms in this molecule lie in the same plane. The ability of Tr^- to bridge two metal ions is thus established.

CONCLUSIONS

The diversity of opinion regarding the mechanism of the "metal-metal" interaction in copper(II) alkanoates indicates that more work, both theoretical and experimental, is needed. Probably one of the more fruitful lines of research would involve assignments of electronic transitions in tetra- and pentacoordinate copper(II), inasmuch as any theoretical treatment of the bonding in copper(II) complexes must begin with a Stark splitting pattern for the d-levels. The effects of σ- and π-covalency in copper(II) alkanoates should be experimentally studied, in order that the theoretical models might be more complete. It is probable that other binuclear complexes will provide experimental information pertinent to the problem. Finally, the importance of Kramers' superexchange in binuclear complexes bridged by more than one atom should be assessed.

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THE USE OF HIGH-SURFACE-AREA-SILICA GELS FOR OBSERVING AND MEASURING ION-SOLVATION

Kenneth C. Williams July 28, 1964

One of the difficult problems encountered in the study of electrolyte solutions is the nature of ion-solvent interactions. In order to understand and describe these solutions in detail, several questions need to be answered. Does the bare ion exist in solution or does it carry with it solvent molecules sufficiently bound to be regarded as part of the ion? If solvent molecules are firmly bound, how many such molecules are "attached"?

The importance of the above questions is realized when notice is taken of the various methods which have been used to study and measure ion-hydrate radii. Some of these methods are theoretical calculations (1), freezing point lowering (2), density and viscosity measurements (3), partial molal volumes (4), compressibility of electrolytic solutions (5), isotopic exchange (6), conductance and diffusion (7), geometric effects at the solution-surface interface (8,9,10,11).

In this seminar, the last two methods will be discussed with emphasis on the last method cited.

CONDUCTANCE AND DIFFUSION

The transport processes of conductance and diffusion are unique in providing ionic parameters directly from experimental measurements. By means of the relations of G. G. Stokes and of Stokes and Einstein, the radii of migrating or diffusing species may be calculated using the equation given by Nightingale (7):

$$r_s = 0.820\ z/\eta^{o}\ \lambda^{o} = 0.732 \times 10^{-9}\ T/D^{o}, \qquad (1)$$

where z is the absolute charge of the ion, λ^{o} is the limiting ionic equivalent conductance, η^{o} is the viscosity of the solvent, T is the absolute temperature, and D^{o} is the limiting ionic diffusion coefficient. However, Stokes' law radii, which are calculated from limiting equivalent conductances, are often inappropriately small because water is not a continuous medium and because the radii of the water molecules usually are not sufficiently large compared with that of the hydrated ions for the conditions of viscous flow to be fulfilled. In order to measure effectively the deviations from Stokes' law for small ions, Nightingale established a calibration procedure based upon ions whose radii in solution are known and, consequently, upon the crystal radii of ions which are unhydrated. By assuming that the large tetraalkylammonium ions possess a sufficiently small surface charge density to be unhydrated, he prepared a calibration curve by plotting r_x/r_s vs. r_s, where r_x is the crystal ionic radius and r_s is the Stokes' radius of the tetraalkylammonium ions. The radii obtained by Nightingale for many ions are given in Table 1 for comparison to values obtained by the following method.

GEOMETRIC EFFECTS AT THE SOLUTION-SURFACE INTERFACE

Introduction

If, in solution, two species of different radii are allowed to come in contact with a high-surface-area silica gel, an increase in concentration of the larger species will occur in the bulk solution (providing reaction with surface is prevented). This is due to a geometric effect which occurs whenever spheres of unequal size contact a surface. This phenomenon has been observed in several systems (12, 8, 13, 9, 11) but in some systems was not recognized (14, 15, 16).

Calculation of Size

If V_A and V_B are the volumes available to the smaller (solvent) and larger (ion-hydrate) species, respectively, and c_i is the concentration of the larger species in a boundless system, and c_f the concentration after contact with the surface then (11)

$$\frac{c_i}{c_f} = \frac{V_B}{V_A} \qquad (2)$$

The pores of the silica gel are assumed to be cylindrical so that the volume available to the larger species is

$$V_B = V_A - P_A W + W \pi \sum_j l_j (r_j - r_B)^2$$

where the pore size distribution is approximated by a series of pores of length l_j and radius r_j, with $r_j > r_B$, and where V_A is the volume of solution mixed with weight W of gel whose pore volume per unit weight (the volume species A penetrates) is P_A. For a weight W of gel, the summation term represents the volume inside the pores available to species B, and the term $V_A - P_A W$ represents the volume outside the pores. The pore volume per unit weight available to species A in the jth pore is given by equation (4).

$$P_{Aj} = \pi l_j (r_j - r_A)^2 , \qquad (4)$$

where $r_j > r_A$. Determination of the pore volume distribution as a function of pore radius frequently depends upon the use of the Kelvin equation. To lend validity to its use in the micropore region, the area under the distribution curve was normalized to P_A, where A refers to the solvent (11). Then P_{Aj} is the area of the jth element of the area under the pore volume distribution curve.

Combining equations (2), (3), and (4), equation 5 is obtained

$$\frac{c_i}{c_f} = 1 - (W/V_A) \left[P_A - \sum_j \frac{P_{Aj}(r_j - r_B)^2}{(r_j - r_A)^2} \right] \qquad (5)$$

where only the pores in which $r_B > r_j$ are considered. For convenience of calculation, equation (5) can be rearranged to

$$\frac{c_i}{c_f} = 1 - (W/V_A) \quad (P_A - Q_1 r_B^2 + Q_2 r_B - Q_3) \quad , \qquad (6)$$

where $Q_1 = \sum_j Q_j$, $Q_2 = \sum_j 2r_j Q_j$, $Q_3 = \sum_j r_j^2 Q_j$, and $Q_j = P_{Aj}/(r_j - r_A)^2$

The Q coefficients of equation (6) were calculated for each solid from the pore volume distributions for both r_A = 1.7 Å and 2.0 Å. For water the value of r_A = 1.7 Å is a lower limit, since for Cs^+, which sees the same volume as water (8), the crystal radius is 1.69 Å. The arbitrary choice of r_A = 2.0 Å is based on the assumption that Cs^+ is slightly hydrated.

Experimental

The following procedure was used in a typical experiment (8); V ml. of solution having a concentration of c_i, was mixed with W g. of silica gel. After equilibrium was obtained (usually 48 hours), the external solution was analyzed to obtain c_f. This was repeated at several concentrations and c_i/c_f was extrapolated to infinite dilution to avoid concentration effects.

The distribution of pore volume with pore radius was determined by the method of Cranston and Inkley (17) from the nitrogen adsorption isotherm at liquid nitrogen temperature. The isotherms were determined with a sorptometer, which uses the gas chromatography principle (18). The BET surface areas (19), were determined using the sorptometer.

Results and Discussion

The ion species whose "size" is measured by the use of the geometric effect is the kinetic entity which collides with the uncharged gel surface and is thereby stripped of some of its water of solvation. Solvate radii, r_B values, are given for three gels in Table I. The value of 2.0 Å for r_A is chosen; r_B is slightly different if the value of 1.7 Å is chosen. Although c_i/c_f is measured for an electrolyte, the r_B value usually can be assigned to one of the ions. Thus, since c_i/c_f = 1 for $CsNO_3$, the value for any other nitrate (always less than unity) can be used to determine cation size; similarly, with other cesium salts anion size can be determined.

In general, for the r_B values given it is concluded that (1) the values for different ions on a given gel have a logical relationship to one another, i.e., the ions generally thought to hydrate more are indeed those with the larger r_B values, (2) the values for a given ion on different gels are in poor agreement, and (3) the values are within the range found using other methods. The geometric effect method of determining size may not be as accurate as some other

methods. However, all methods of determining size are of interest because each method defines uniquely the nature of the quantity being measured. No present method gives information about the size of the solvate when it is in the vicinity of a wall. Another advantage of the exclusion method is that it can be used under rather unusual conditions, e.g., in concentrated acid solutions, and over a wide temperature range.

Table I. Summary of Ion Solvate Radii

Ion	r_B, Å			
	Code 70[a]	Code 40, W. W.[b]	Code 40, A. W.[c]	Radii Nightingale(7)
H^+	---	4.0	5.0	2.82
Li^+	5.1	4.1	6.7	3.82
Na^+	4.8	4.0	---	3.58
K^+	3.4	3.3	5.0	3.31
Rb^+	---	2.6	---	3.29
Cs^+	---	(2.0)	---	3.29
Be^{++}	---	5.4	---	4.59
Mg^{++}	5.4	4.3	---	4.28
Ca^{++}	---	4.2	---	4.12
Sr^{++}	5.8	4.1	---	4.12
Ba^{++}	---	4.4	---	4.04
Al^{+++}	7.0	5.0	6.3	4.75
In^{+++}	---	5.3	---	---
Cr^{+++}	5.7	5.3	6.4	4.61
Mn^{++}	---	4.1	---	4.38
Fe^{+++}	---	---	7.3	4.28
Co^{++}	5.6	4.8	---	4.23
Ni^{++}	---	4.6	6.8	4.04
Cu^{++}	---	4.3	4.9	4.19
Y^{+++}	---	---	5.9	---
Ag^+	---	3.8	---	3.41
La^{+++}	---	---	5.9	---
Ge^{+++}	---	---	5.8	---
Pr^{+++}	---	---	5.8	---
Nd^{+++}	---	---	5.5	---
Sm^{+++}	---	---	6.0	---
Gd^{+++}	---	---	5.6	---
Th^{+4}	---	---	6.6	---
UO_2^{++}	---	4.1	6.3	---
Cl^-	---	---	2.7	2.10
Br^-	---	---	3.4	3.30
I^-	---	---	3.8	3.30

a. P_A = 1.15 ml/g; Surface area = 352 m^2/g.
b. P_A = 0.40 ml/g; Surface area = 594 m^2/g.
c. P_A = 0.40 ml/g; Surface area = 498 m^2/g.

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HYDRIDO COMPLEXES OF TRANSITION METALS

Mahdi N. Al-Zagoum August 4, 1964

INTRODUCTION

It has been long recognized that all elements, except the transition metals(1,2), form hydrides in which the hydrogen can form a bond with the metal atoms. These hydrides have been classified as those formed by electropositive elements and are said to be ionic, e.g., NaH, KH; and those formed by electronegative elements and are said to covalent and volatile, e.g., H_2O, H_2S. The salt-like hydrides(2), e.g., AlH_3 are considered to be between these two types. Up to 1952, no molecular transition-metal hydrides were known except $[FeH_2(CO)_4]$ and $[CoH(CO)_4]$(1,2) which are volatile but very unstable, decomposing even at -20°C, and which behave as weak acids in water. The situation before 1952 is illustrated in Fig. 1 from which it will be seen that the main gap in the hydride chemistry falls among the transition elements.

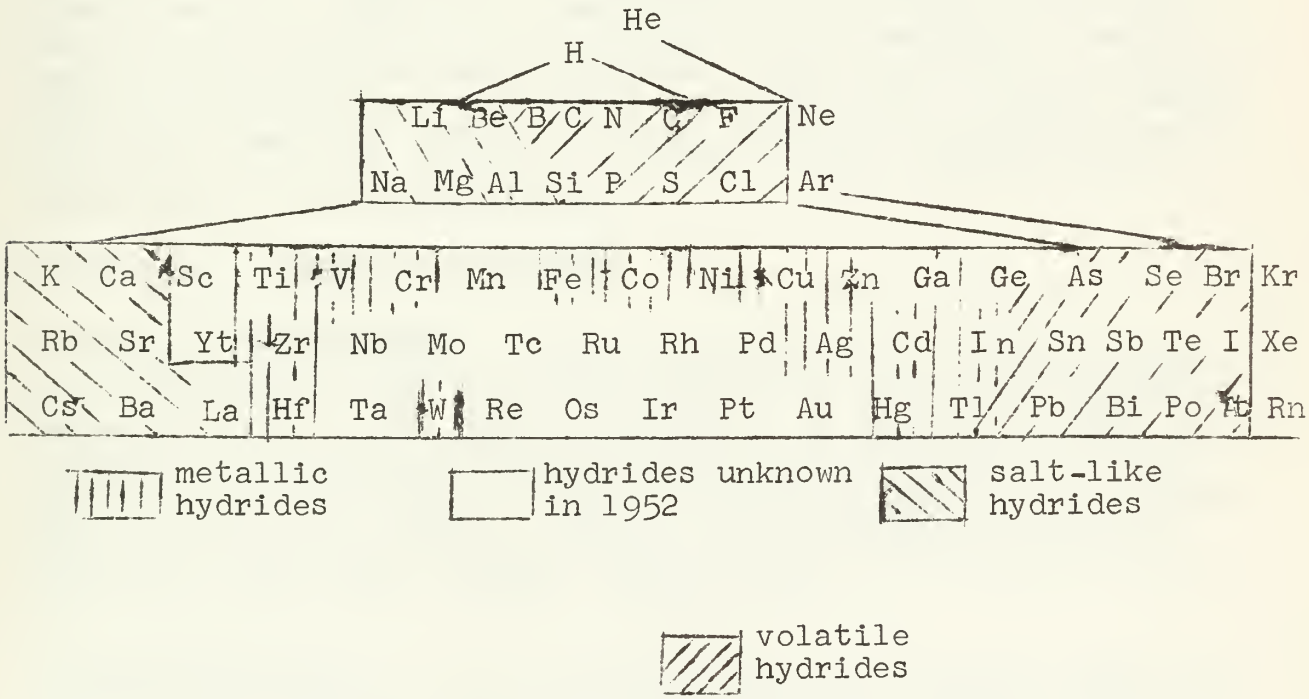

Figure 1. Elements were known in 1952 to form simple hydrides

However, in 1955, $[ReH(C_5H_5)_2]$(3,4,5) was discovered by accident during the attempted preparation of biscyclopentadienylrhenium. This discovery was followed in 1957, by the discovery of transition-metal hydrides which were stabilized by tertiary phosphines (1,2)e.g., <u>trans</u>-$[Pt(H)Cl(PEt_3)_2]$ and which were stable enough to

allow complete study of the nature and properties of the coordinated hydride ion. In 1960, a new type of hydrido complex stabilized by tertiary phosphines or tertiary arsines, and carbon monoxide, e.g., $[Ir(H)Cl_2(CO)(Ph_3P)_2]$(23) or $[Ru(H)Cl(CO)(PEt_2Ph)_3]$(25) was discovered; this type was considered to be the more stable.

The scope of this seminar will be limited to a discussion of the bonding and properties of the hydrogen in these complexes with brief reference to the preparative methods.

The general formula of the hydrido-complexes of transtion metals can be either $[M_mH_nL_p]$(1) or $[MH_xX_yL_z]_n$(2), where M is a transition metal atom; L is an effective ligand of high-field strength (ohter than hydrogen) which can stabilize the metal-to-hydrogen bond, e.g., CO, NO, CN^-, tertiary phosphine, and cyclopentadienyl ion; n is usually equal to one or sometimes equal to two as in $[FeH_2(CO)_4]$; and x is a univalent anionic ligand as halide ion. The complexes having these formulas are usually nonelectrolytes(1,2,6,8) and diamagnetic (i.e., the metal d-electrons are paired under the influence of the high-field strength of the ligand L). The metal atom in these complexes usually has the effective atomic number of the next inert gas. The metal-to-hydrogen bond is shorter than the radius sum(9,10) because of the very close association of the hydrogen to the metal which appears to be bonded directly to it. Some of these complexes behave as acids(9,11), e.g., those derived from group VI metals; and some behave as bases(11), e.g., $[ReH(C_5H_5)_2]$, $[MoH_2(C_5H_5)_2]$, and $[WH_2(C_5H_5)_2]$.

PROPERTIES OF HYDRIDO COMPLEXES

Ligand-field Strength:

The hydrido ligand in these complexes has a large ligand-field strength. That is, the bands due to d → d transitions are shifted to the ultraviolet region. An example to that is in trans-$[RuCl_2(PMe_2CH_2CH_2PMe_2)_2]$ the d → d transition occurs at 411 mμ, but in trans- $[Ru(H)Cl(PMe_2CH_2CH_2PMe_2)_2]$ this transition occurs below 364 mμ. This is why the hydride ion was classified with those groups, such as methyl and cyanide ion, that have high-ligand field strength(13).

Thermal Stability:

It is known that the highest element in a group forms the most stable hydride(1,9,12). This is found to be true in a series of compounds of the type $[MHC_5H_5(CO)_3]$ where M = Cr, Mo, and W, but that is not true for the carbonyl hydrides(12) where $[MnH(CO)_5]$ is more stable than $[ReH(CO)_5]$. However, the order of stability(1,2) of these compounds lies in the sequence: carbonyl hydrides < cyclopentadienyl hydrides < cyclopentadienyl carbonyl hydrides < tertiary phosphine hydrides. These facts are observed for the nickel group of compounds, which have the

formula $[M(H)Cl(PEt_3)_2]$; the platinium compound(12) is very stable and can be easily isolated, but the corresponding nickel compound has never been isolated. Another example is given in table I.

Table I

Thermal stability of compounds of the type $[M(H)Cl(Et_2PCH_2CH_2PEt_2)_2]$

M	Decomposition point, °C	Melting point, °C
Fe	155	155
Ru	310	175
Os	315	171

Nuclear magnetic resonance spectra:

The hydride ion in these complexes has a very large chemical shift(9,14,15) towards high fields as shown by NMR spectra (table II).

This large shift might indicate high electron density at the proton. Also it can be explained by the large shielding effects caused by the field generated by a paramagnetic electron circulation which is induced by the applied magnetic field in the non-bonding d-electrons at the metal atom. However, this large shift cannot primarily be attributed to S electrons(9) of the hydrogen.

Table II

Proton chemical shift in p.p.m. of the hydride ion in some hydrido complexes relative to benzene

Compound	Chemical shift	Reference
trans-$[Pt(H)Cl(PEt_3)_2]$	22.4	2
trans-$[Pt(H)Br(PEt_3)_2]$	20.9	2
trans-$[Pt(H)I(PEt_3)_2]$	18.0	2
$[CrH(C_5H_5)(CO)_3]$	13.1	9
$[MoH(C_5H_5)(CO)_3]$	12.8	9
$[WH(C_5H_5)(CO)_3]$	14.7	9
$[ReH(C_5H_5)_2]$	20.5	9
$[FeH_2(CO)_4]$	17.4	9
$[CoH(CO)_4]$	17.3	9

This large shift for the hydride ion is considered to be well separated(14) from that due to the protons in the organic part of the molecule as shown by the following spectra in Figures 2 and 3 for the compounds $[Pt(H)Cl(PEt_3)_2]$(2) and $[Ru(H)I(chelate)_2]$(14), respectively, where chelate is $C_2H_4(PMe_2)_2$, $C_2H_4(PEt_2)_2$, or o-$C_6H_4(AsMe_2)_2$.

Figure 2. NMR spectrum of trans-$[Pt(H)Cl(PEt_3)_2]$ in CCl_4.

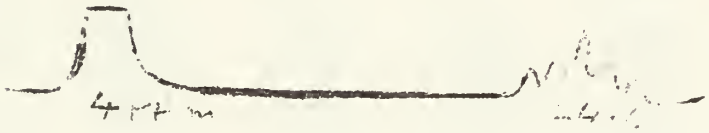

Figure 3. NMR spectrum of trans-$[Ru(H)I(PMe_2CH_2CH_2PMe_2)_2]$ in CH_3Cl.

The low-field line in Fig. 2 represents the chemical shift of the organic ligand protons, and the high-field line represents the chemical shift of the hydrogen attached to the metal atom. The high-field line is split into a triplet by the two equivalent phosphorous nuclei (spin = 1/2). In Fig. 3, the high-field resonance line is split into five sharp, equally spaced lines (intensity ratio 1:4:6:4:1) by the coupling of the four equivalent phosphorous nuclei of the chelate groups with the hydrogen nucleus.

Infrared spectra:

Infrared spectra of these compounds has a strong absorption band(16,17,18) characteristic of the metal-to-hydrogen stretching frequency in the region 1700-2000 cm^{-1}, and another band characteristic of the metal-to-hydrogen bending vibration in the region 600-900 cm^{-1}. The metal-to-hydrogen stretching frequencies for a number of hydride compounds are shown in table III.

Table III

Stretching frequencies in cm^{-1} of the metal-to-hydrogen bond for some hydrido complexes

Compound	ν M-H	Reference
$[(C_5H_5)_2MoH_2]$	1847	11
$[(C_5H_5)_2WH_2]$	1896	11
$[(C_5H_5)_2TaH_3]$	1735	11
trans-$[FeH_2\{o\text{-}C_6H_4(PEt_2)_2\}_2]$	1726	2
$[M(H)Cl(Et_2PCH_2CH_2PEt_2)_2]$		
M = Fe	1849	1
= Ru	1938	1
= Os	2039	1

The hydrogen in these compounds is sensitive to its environments(2) and, consequently, the stretching frequency of M-H bond will be affected by other ligands attached to the metal atom. This situation for platinium complexes(19,20) of the formula $[(ER_3)_2Pt(H)X]$ is illustrated in table IV.

Table IV

The effect of various anionic ligands on the metal-to-hydrogen stretching frequency, cm^{-1}, for compounds of the type $[(ER_3)_2Pt(H)X]$

ER_3	NO_3	Cl	Br	I	NO_2	SCN	CN
PMe_3		2182					
PEt_3	2242	2183	2178	2156	2150	2112	2041
$PPhEt_2$	—	2199		2179	—		—
$AsEt_3$	—	2174	2167	2139	—	2108	—

The anionic ligands in table IV are placed in the order of increasing trans-effect and also in the order of decreasing metal-to-hydrogen stretching frequencies and decreasing metal-to-hydrogen bond strength. It can be seen that the stretching frequency of the metal-to-hydrogen decreases in passing from chlorine to iodine; this can be explained by the fact that iodine, by the mesomeric effect which is caused by platinium II ion, attracts the electrons more than the chlorine does and hence the M-H stretch is decreased with iodine. This effect, (table V), is completely different(18) for the compounds of the type $[M(H)X(diphos)_2]$ where M = Fe, Ru, or Os; X = halide ion; and diphos = $PEt_2CH_2CH_2PEt_2$.

Table V

The effect of halide ions on the metal-to-hydrogen stretching frequency for the compounds indicated

Compound	x = Cl	I
$[Fe(H)X(diphos)_2]$	1849 cm^{-1}	1872 cm^{-1}
$[Ru(h)X(diphos)_2]$	1938	1948
$[Os(H)X(diphos)_2]$	2039	2051

The effect in compounds of table V is mostly an inductive effect by which the chlorine is more effective than iodine in attracting the electrons and hence the M-H stretching frequency is decreased with chlorine. The order of decreasing the M-H stretching frequencies for the iridium compounds (6,7,8) of the type $[Ir(H)Cl_2(ER_3)_3]$ where ER_3 is Ph_3P, Ph_3As, or Ph_3Sb lies in the sequence: $(Ph_3P)_3 > (Ph_3As)_3 > (Ph_3Sb)_3$.

The metal-to-hydrogen stretching frequency was also found to be susceptible to the nature of the solvents in which the spectra

are measured (2,16). Higher frequency was reported with polar solvents. Table VI shows the $\Delta\nu_{M-H}$ values (where $\Delta\nu_{M-H}$ = ν M-H chloroform $\bar{\nu}$ M-H hexane) for the compounds indicated.

Table VI

Effect of the solvent on the M-H stretching frequencies.

	Compound	ν M-H hexane	$\Delta\nu$ M-H
I	trans-$[Pt(H)Cl(PEt_3)_2]$	2183 cm^{-1}	30 cm^{-1}
II	trans-$[Ir(H)Cl_2(PEt_3)_3]$	2090	7
III	Cis-$[Ir(H)Cl_2(PEt_3)_3]$	insoluble	35
IVa	$[IrH_2Cl(PEt_2Ph)_3]$*	2162	34
IVb	$[IrH_2Cl(PEt_2Ph)_3]$**	2026	0
V	trans-$[IrHCl_2(AsEt_3)_3]$	2099	0

*Hydrogen atom is trans- to chlorine
**Hydrogen atom is trans to a trisubstituted phosphine.

These values indicate that $\Delta\nu_{M-H}$ is large when the hydrogen is trans to chlorine; the hydrogen in this case is solvent sensitive, but solvent insensitive when it is trans to a trisubstituted phosphorous or arsine (IVb and V in table VI).

PREPARATION

In general, these compounds are prepared(11,22,24) by the interaction of the anhydrous halides with a solution of the desired ligand in a suitable solvent, or by the reduction(17,18) of the corresponding halogeno-complexes by some reducing agents in solvent media. It is believed that the solvent acts as a proton-transfer agent. Various reducing agents and solvent media have been used, including lithium aluminium hydride in tetrahydrofuran, alcoholic potassium hydroxide, alcoholic hypophosphorous acid, aqueous hydrazine, and even molecular hydrogen(23,28) in benzene. Compounds(15) of the type $[(C_5H_5)_2MH_x]$ were prepared according to the following equation:

$$[(C_5H_5)_2TaCl_3] \xrightarrow[\text{THF}]{\text{NaBH}_4\text{ in}} [(C_5H_5)_2TaH_3]$$

Other compounds were prepared as follows:

$$(NH_4)_2IrCl_6+Ph_3P \xrightarrow{\text{alcohol}} [Ir(H)Cl_2(Ph_3P)_3] \quad (7)$$

$$Cr(C_5H_5)_2+CO+H_2 \xrightarrow{\text{high pressure}} [CrH(C_5H_5)_2(CO)_3] \quad (2)$$

$$Fe(C_5H_5)(CO)_2Cl \xrightarrow[\text{in THF}]{\text{NaBH}_4} [FeH(C_5H_5)(CO)_2] \quad (19)$$

$$\text{Cis- or trans-}[PtCl_2(PEt_3)_2] \xrightarrow[\text{KOH}]{\text{alcoholic}} \text{trans-}[Pt(H)Cl(PEt_3)_2] \quad (24,25)$$

$$\text{Cis- or trans-}[PtCl_2(PEt_3)_2] \xrightarrow[\text{THF}]{\text{LiAlH}_4} \text{trans-}[Pt(H)Cl(PEt_3)_2] \quad (19)$$

$$[PtCl_2(PR_3)_2] \xrightarrow{\text{aq.}N_2H_4} \text{trans}[Pt(H)Cl(PR_3)_2] + N_2+N_2H_5Cl \quad (1)$$

$$[IrCl_3(PEt_3)_3] \xrightarrow{\text{alcoholic KOH}} [Ir(H)Cl_2(PEt_3)_3] \quad (25)$$

$$[Ru_2Cl_3(PEt_2Ph)_6]Cl \xrightarrow{\text{alcoholic KOH}} 2[Ru(H)Cl(CO)(PEt_2Ph)_3] \quad (25,26)$$

$$[RuCl_2(PMe_2CH_2CH_2PMe_2] \xrightarrow[\text{THF}]{LiAlH_4} [Ru(H)Cl(PMe_2CH_2CH_2PMe_2)_2] \quad (14,18)$$

$$[Ir^{I}Cl(CO)(PPh_3)_2] \xrightarrow[\text{at } 25^{o}]{H_2 \text{ in benzene}} [Ir^{III}H_2Cl(CO)(PPh_3)_2] \quad (23)$$

$$[Rhen_2Cl_2]^{+} \xrightarrow{BH_4^-} [Rh\ en_2(H)Cl]^{+} + Cl^{-} + 1/2B_2H_6 \quad (27)$$

BONDING AND STRUCTURE

The most significant information about the structure and bonding of these compounds comes from the high-resolution nuclear magnetic resonance studies on the compound $[(C_5H_5)_2TaH_3]$(15) whose spectrum was reported to contain: Aresonance line (relative intensity = 10) at T = 5.25, assigned to the ten equivalent protons in the two C_5H_5 groups; a triplet (relative intensity = 1) at T = 11.63; and a doublet (relative intensity = 2) at T = 13.08. The triplet and the doublet resonance lines that occur on the high-field side relative to tetramethylsilane indicate the presence of three protons attached to the metal atom(4,29); two protons are in equivalent environments, while the third is different. Hence, it is considered that all of the compounds $[(C_5H_5)_2MH_x]$ have three orbitals that are not involved in the metal-to-ring bonding(11,22), two orbitals are equivalent, these are the A-labeled orbitals in Figure 4.

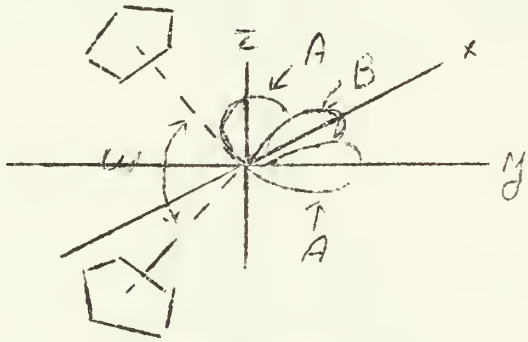

Figure 4. The bonding scheme of the compound $[(C_5H_5)_2TaH_3]$.

All three orbitals are available for bonding to hydrogen or for occupation by lone pairs of electrons. In the compound $[(C_5H_5)_2TaH_3]$, all these orbitals are involved in bonding to the hydrogens, but in the compound $[ReH(C_5H_5)_2]$ only one orbital is used by hydrogen and in the compounds $[(C_5H_5)_2MoH_2]$, $[(C_5H_5)_2WH_2]$, and $[(C_5H_5)_2ReH_2]^{+}$ two orbitals are used; the remaining orbitals are filled by low pairs of electrons. These facts explain why the compound $[(C_5H_5)_2ReH]$ and possibly $[(C_5H_5)_2MoH_2]$, $[(C_5H_5)_2WH_2]$ behave as bases, while the compounds $[(C_5H_5)_2TaH_3]$ and $[(C_5H_5)_2WH_3]^{+}$ do not show any basic behavior.

The two metal-to-ring axes(31,10) are believed to be at an angle W to each other, (Fig. 4) except the neutral ferrocene-like compounds. However, x-ray structure determination indicated this angular situation (30) for the cyclopentadienyl rings in the compound $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$. This was also said(10,15) to be possible in the range $135^{o} \leq W \leq 80$ since there is a little loss in the metal-to-ring bounding energy and consequently this binding

energy becomes not very dependent on whether the rings axes are collinear or angular.

The non-linearity of the rings was confirmed(10) by the single crystal x-ray analysis of the compound $[(C_5H_5)_2MoH_2]$ which shows that this molecule is "wedge-like" as in Fig. 5, and the angle between the rings is $25^\circ \pm 3^\circ$. The bond angle H-Mo-H is $90^\circ \pm 10^\circ$, and the estimated Mo-H bond distance ($1.1 \pm 0.2A^\circ$) is less than the radius sum which indicates that the hydrogen in these compounds is bound directly to the non-bonding d-electrons of the metal atom(9).

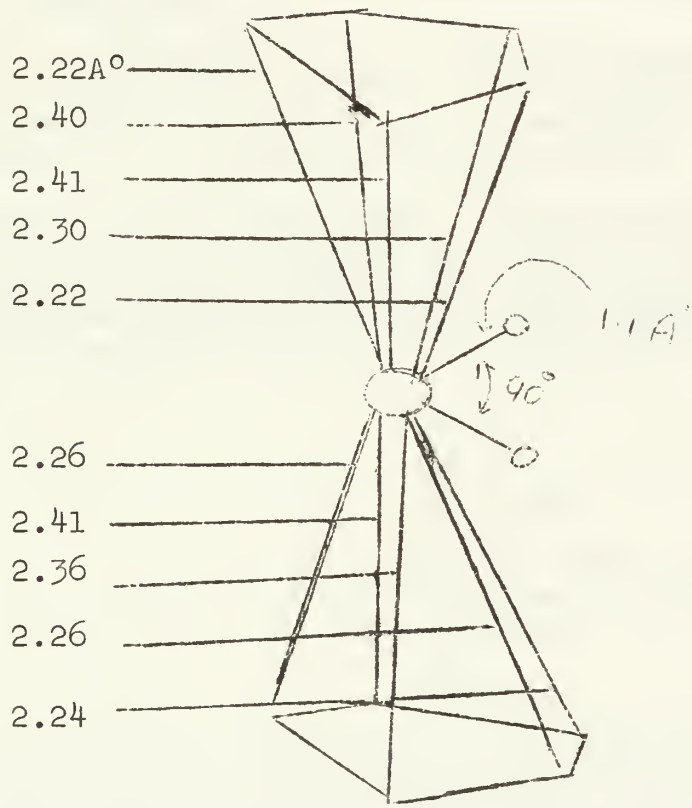

Figure 5. Structure of the molecule $[(C_5H_5)_2MoH_2]$

On the basis of the last argument, the hydrogen might be located between the ring and the metal atom(1,4). This gives three possible types of structure to the compound $[ReH(C_5H_5)_2]$ and also to its cation $[ReH_2(C_5H_5)2]^+$ as shown in Fig. 6.

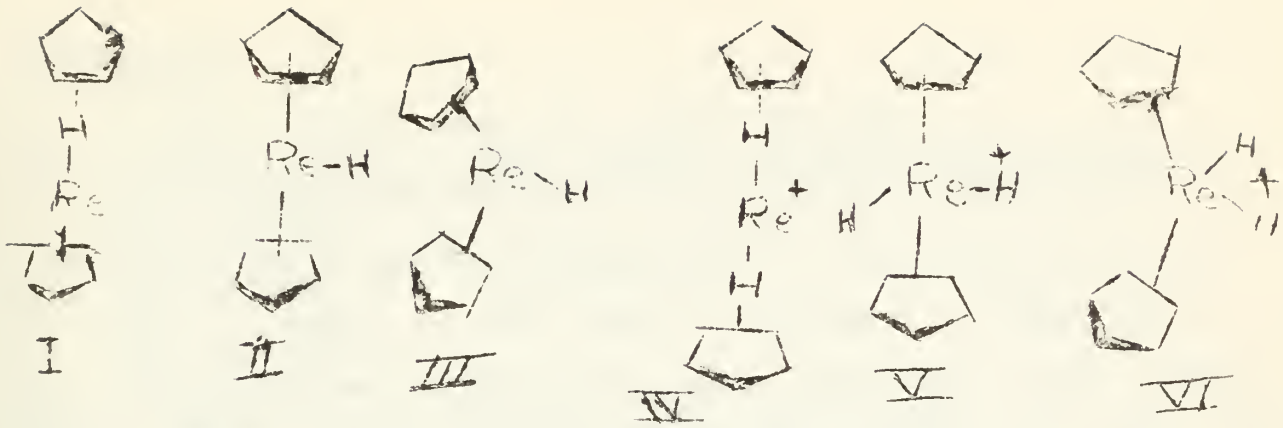

Figure 6. Structures of the compounds $[ReH(C_5H_5)_2]$ and $[ReH_2(C_5H_5)_2]^+$

Structure I is considered to be unlikely because the two rings are not in the same environments. In structure II, the rings are aligned and in III are likely to represent the molecule since the two rings are in equivalent environments.

Compounds of the type <u>trans</u> - $[Pt(H)X(PR_3)_2]$(2), (where x is halide), in which the hydrogen was proved to be present as an anionic ligand, have been shown by x-ray structure determination to have a planar structure for the heavy ligands and the hydrogen was shown to complete the square coordination, Fig. 7.

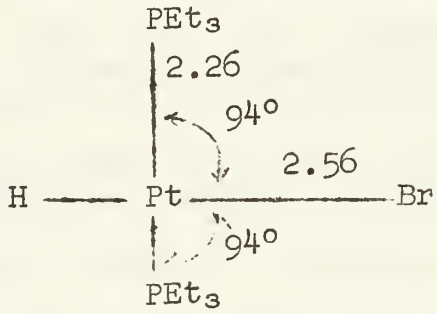

Figure 7. Structure of the compound $[Pt(H)Br(PEt_3)_2]$

The Pt-P bond distance is less than the radius sum because of the partial double bond character, while the Pt-Br bond distance is greater than the radius sum because of the ionic character and the polarity of this bond caused by the presence of the hydride ion which is in the position trans to the bromine.

CONCLUSION

It can be concluded that the hydrido complexes have now been established for a large number of transition metals, and hydrogen atoms attached to transition metals can be easily detected by the nuclear magnetic resonance technique which makes the metal-to-hydrogen bond more familiar and common than was previously thought. One of the characteristics of these compounds is the high-field shift observed for the protons by this technique.

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SOME ORGANOMETALLIC CHEMISTRY OF GROUP IIB

Larry M. Seitz November 17, 1964

Introduction

Diethylzinc and ethylzinc iodide, first prepared by Frankland in 1849 (1), were the first truly organometallic compounds reported. Actually the simple organozinc compounds have a notable place in the history of chemistry, since studies on their vapor densities and chemical reactions led Frankland to postulate the first clear valence theory in which he suggested each element had a definite limited combining capacity (2). Frankland used diethylzinc so widely to make other organometallic compounds that he may properly be called the founder of the chemistry of organometallic compounds (3).

Frankland's original method for the preparation of dialkylzinc compounds involves the thermal decomposition of alkylzinc iodides, the latter being prepared by direct reaction of alkyl halides with a zinc-copper alloy. The alkylzinc compounds are distilled from the reaction mixture. Improvements include the use of a special zinc-copper alloy and high boiling ethers as solvents (4).

Coates (4) has compiled a wealth of information concerning the preparations of the organometallic compounds of this group and this reference provides a good source to the early literature. Some of the more common general methods are summarized below.

The dialkyls or diaryls of this group can be obtained by the reaction of the anhydrous metal halides with a Grignard solution.

$$MX_2 + \underset{\text{(excess)}}{2RMgX} \xrightarrow{\text{ether}} R_2M + MgX_2$$

The more volatile dialkyls may be distilled from the reaction mixture. Organozinc compounds can be prepared by heating zinc metal with the appropriate organomercury compound. However, with

$$Zn + R_2Hg \rightarrow R_2Zn + Hg$$

cadmium an equilibrium results. The diaryls of zinc and cadmium

$$Cd + R_2Hg \rightleftharpoons R_2Cd + Hg$$

can be obtained by the reaction of the metal halides with aryllithium reagents in ether. Both dialkyls and diaryls of mercury can be prepared from sodium amalgam and the appropriate halide diluted with xylene.

$$RX + Na(Hg) \rightarrow R_2Hg + NaX$$

The dialkyl compounds of this group are all volatile liquids, e.g., the boiling points for Me_2Zn, Me_2Cd, and Me_2Hg are 44°, 105.5, and 92°C, respectively. The diaryls are all solids. Sensitivity to air varies considerably with dimethylzinc being spontaneously inflammable in air, dimethylcadmium only inflammable when a large surface area is exposed, and finally dimethylmercury does not react at all with oxygen or water under normal conditions. On the other hand, the thermal stability of the dialkyls decreases in the order $R_2Zn > R_2Cd > R_2Hg$.

Structure and Bonding

The dialkyls and diaryls of this group are monomeric and have linear structures. Infrared and Raman spectra of Me_2Hg and Me_2Zn support a linear C-M-C structure with essentially free rotation of the methyl groups (5). Also an X-ray structure study of Me_2Zn by Rundle (6) shows that the crystal consists of linear monomers. Linear structures, of course, are in agreement with the metal atoms using sp orbitals in bonding to the organo-groups.

At this point, however, it is necessary to note that mercury has a special tendency to form compounds in which the metal is attached to only two ligands. Orgel (7) has attributed this to d-s mixing rather than to the special stability of sp-hybrid bonds. As the data in Table I indicates, the s-p separation in Hg is slightly greater than in Zn or Cd, but it is thought it is not large enough to account for the large extra stability of the linear structure. On the other hand, the energy of the lowest d^9s state above the d^{10} ground state for mercury is only about one half the value for cadmium or zinc, and is even less than the s-p separations. Although some sp hybridization cannot be completely excluded, it must also be supposed that mercury uses a combination of one 6p orbital and one d-s orbital (mixing of the 5dz orbital with the 6s orbital) in its bonding to the organo-groups.

Table I

	Energy (cm^{-1}) of lowest d^9s state above the d^{10} ground state (M^{++} ions)	E (s-p) of M^+ (cm^{-1})
Zn	78,105	49,000
Cd	80,463	45,800
Hg	42,862	57,600

Coordination Complexes

An indication of the existence of coordination complexes was the observation made in 1859 by Frankland (8) that the use of dimethyl or diethyl ether as a solvent greatly facilitates the formation of dimethylzinc from zinc and methyliodide, and that separation from the solvent proved to be impossible. However, no one seemed to pay much attention to this, and in fact even for many years it was generally thought that organozinc or organocadmium compounds were unable to form neutral donor-acceptor complexes. Recently examples of coordination complexes have been reported and most of these are listed in Tables II and III.

Table II

Coordination Complexes of Me_2Zn and Me_2Cd

Complex	M.P. °C	B.P. °C	Ref. No.	Remarks
$Me_2Zn \cdot NMe_3$	-52	84	28	
$Me_2Zn \cdot 2NMe_3$	84	-	28	
$Me_2Zn \cdot NEt_3$	95	-	28	Dissociates in benzene
$Me_2Zn \cdot C_5H_5N$	44	-	28	" " "
$Me_2Zn \cdot TEED$[a]	66	-	28	Does not dissociate in benzene
$Me_2Cd \cdot TMED$[b]	80	-	11	Dissociates readily
$Me_2Zn \cdot Bipy$[c]	-	-	28	Can be vacuum distilled
$Me_2Cd \cdot Bipy$	-	-	11	High dissociation pressure at room temp
$Me_2Zn \cdot Phenan$[d]	-	-	28	Can be vacuum distilled
$Me_2Cd \cdot Phenan$	-	-	11	Decomposes above 85°
$Me_2Zn \cdot OMe_2$	-	46	12	Distills without decomposition
$Me_2Zn \cdot O(CH_2)_2$	-	47	12	Distillable at atmospheric pressure
$Me_2Zn \cdot O(CH_2)_3$	-2.5	-	12	Distillable at atmospheric pressure
$Me_2Zn \cdot 1.2\ O(CH_2)_3$	-	80	12	This composition distills at 80°
$Me_2Zn \cdot 2\ O(CH_2)_4$	-	83	12	Distillable at atmospheric pressure

Table II (continued)

Complex	M.P. °C	B.P. °C	Ref. No.	Remarks
$Me_2Cd \cdot O(CH_2)_4$	-	105	11	Distills with some decomposition
$Me_2Zn \cdot 2\ O(CH_2)_5$	-	93.5	12	Distillable at atmospheric pressure
$Me_2Zn \cdot$(1,4-dioxane)	66	-	27	Distills with decomposition
$Me_2Cd \cdot$(1,4-dioxane)	57	-	11	Sublimes at 30° and 5 mm Hg pressure
$Me_2Zn \cdot$(1,4-thioxane)	23.5	-	27	Distills with decomposition
$Me_2Zn \cdot 2$ diglyme[e]	-	91	27	Distills without decomposition, but dissociates in nonpolar solvents to diglyme and the 1:1 chelate adduct
$Me_2Zn \cdot$diglyme	5.5	-	27	Decomp. 75° to Me_2Zn + 1:2 adduct

[a] TEED = N,N,N',N'-tetraethylethylenediamine

[b] TMED = N,N,N',N'-tetramethylethylenediamine

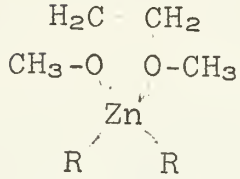
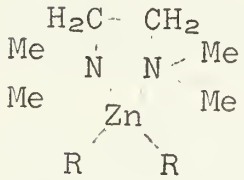
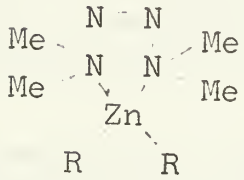
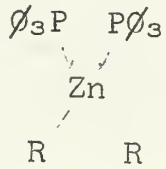
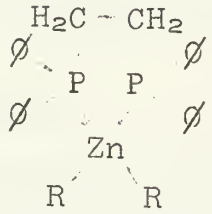
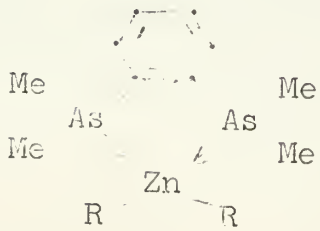
[c] Bipy = 2,2'-bipyridine

[d] Phenan = 1,10-phenanthroline

[e] diglyme = ethyleneglycol dimethyl ether

Table III

Some Coordination Complexes of Other Organozinc Compounds (10)

Complex	R	M.P.
	C_6H_5	60-61
	C_6F_5	108-109
	C_4H_9	liq.
	C_6H_5	123-124
	C_6F_5	161-162
	C_4H_9	-45
	C_6H_5	54-55
	C_6F_5	136-137
	C_6H_5	142-143
	C_6F_5	166-167
	C_4H_9	114
	C_6H_5	185-187
	C_6F_5	211-213
	C_4H_9	liq.
	C_6H_5	132-133
	C_6F_5	136-137

The stability of the neutral donor-acceptor complexes decreases in the order zinc > cadmium > mercury. The coordination complexes of organomercury compounds are so unstable that none have been reported. This stability sequence is probably best illustrated by the behavior of the dimethyl derivatives with bipyridyl, as described by Coates and Green (9). The inability of organomercury compounds to form adducts may be ascribed to (a) stabilization of linear structure by d-s hybridization, (b) decrease in bond strength, (c) high energy of p states.

Noltes and Van Den Hurk (10) have found that increasing the electronegativity of the R group on zinc increases the tendency to form coordination complexes. Diphenylzinc readily forms complexes with ethyleneglycol dimethyl ether (diglyme) and triphenylphosphine, while di-n-butylzinc forms only a very weak complex with diglyme and none at all with triphenylphosphine. Thiele also noted that in going from methyl to ethyl or propyl in R_2Cd, the complexing tendency decreases strongly (11).

In the cyclic ether adducts, $Me_2Zn \cdot O(CH_2)_n$, the strength of the zinc-ether bond and tendency to form 1:2 adducts increases with n (12). The cause of these stability differences probably lies in the orientation and character of the oxygen orbitals, which vary with ring size of the ether. Also these cyclic ether adducts dissociate in solution with the amount of dissociation depending on the solvent.

In the complexes derived from arsenic or phosphorus containing ligands, it appears that $d\pi$-$d\pi$ bonding is not important because the dibutylzinc complexes (Table III) with nitrogen containing ligands are more thermally stable than the ditertiary arsine complexes (10). Lewis and co-workers have recently considered the role of $d\pi$-$d\pi$ bonding in the ditertiary arsine complexes of d^{10} metals unimportant in view of the high ionization potential of the non-bonding d^{10} shell of the metal atoms (13).

All of these adducts are less sensitive to oxygen and water than the free uncomplexed dialkyls.

Anionic Complexes

Wanklyn reported the first anionic complex $NaZnEt_3$ in 1858 (14). Most of these complexes reported up to now are organozinc complexes. A few examples include the anions ZnR_3^- (17,18), ZnR_2H^- (15,16), ZnR_4^{2-} (19), $Zn(C{\equiv}CH)_4^{2-}$ (20), and $Cd(C{\equiv}CH)_4$ (21). Organomercury compounds have very little tendency to form anionic complexes (22).

Exchange Reactions

McCoy and Allred (23) have employed nuclear magnetic resonance along with equations developed by Gutowsky (24) to estimate the rate of methyl group exchange in the systems Me_3Al-Me_2Cd, Me_2Cd-Me_2Zn, Me_2Zn-Me_2Hg, and Me_2Cd-Me_2Hg. In the Me_3Al-Me_2Cd system, with benzene as solvent, rapid exchange occurs and the upper limit of the average lifetime τ_A of a methyl group on a given metal atom is estimated to be 0.09 sec. In the Me_2Cd-Me_2Zn system rapid exchange also occurs, and the rate of exchange depends somewhat on concentration of the components. When the concentrations are greater than about one molar only one peak appears and $\tau_A = 0.03$, but in more dilute solutions two peaks appear corresponding to slower exchange. Using dilute solutions, McCoy and Allred demonstrated that the exchange rate is not greatly affected by solvent which ranged from dielectric constant 2 (cyclohexane) to 36.1 (pure nitrobenzene). It therefore appears that the rate-determining step is not primarily ionic.

In the systems Me_2Zn-Me_2Hg and Me_2Cd-Me_2Hg, two resonance peaks appear with the sharpness and a separation comparable to that estimated from the pure components for no exchange.

Reutov (25), working with diphenylmercury-di-p-chlorophenylmercury^{203}, reported mercury-mercury exchange involving four groups migrating simultaneously, since no RHgR' was found. However, it is not at all clear if Reutov specifically looked for the RHgR' species so this result seems doubtful.

In light of the above results, Dessy and co-workers decided to investigate the exchange pathway in more detail (26). They pictured two possible transition states, drawn out below, where the octahedral form would probably require the transfer of two

Octahedral

S_F2

groups from each metal during one interchange, thus providing no RMR' species, while the S_F2 transition state would give rise to RMR'. By using mass spectrometry to study the particular system

$$(CD_3)_2Hg + (CH_3)_2Mg \xrightarrow{THF}$$

Dessy and co-workers were able to detect the presence of the species CD_3HgCH_3, which suggests the S_F2 transition state is involved.

When mercury is one of the atoms involved, the methyl group exchange rate is slow. Also, coordinating solvents tend to increase the rate of exchange slightly, and this may be due to one or both of the following effects: (1) the activated complex may be stabilized by coordination, or (2) the carbon-metal bond may be weakened by coordination.

New Organometallic Compounds with Hg-Si, Hg-Ge, or Zn-Si Bonds

Bis(triphenylsilyl)zinc, the first compound containing a Zn-Si bond, was isolated by Wieberg and co-workers (29). It was prepared by reacting $KSiph_3$ with $ZnCl_2$ in liquid ammonia. Wieberg also reported the preparation of the compound bis(trimethylsilyl)mercury by shaking liquid Me_3SiBr with Na/Hg for several days. This is also the first compound containing a Hg-Si bond to be isolated, and further the first example of a volatile (sublimable) metal silyl. It is more stable than the corresponding carbon compound $Hg(CMe_3)_3$.

Some Russian workers (30) have reported the preparation of the compound bis(triethylgermanyl)mercury, $(Et_3Ge)_2Hg$, b.p. 118-20°, by heating Et_3GeH with Et_2Hg at 100-120°. However, reaction of Et_3SnH with Et_2Hg does not give the corresponding tin compound but the products Hg, C_2H_6, and Et_6Sn_2 (32).

Also the compounds $EtHgSiEt_2SiEt_3$, $Hg(SiEt_2SiEt_3)_2$, and $Et_3GeHgSiEt_3$ were prepared by some Russian workers (31). The first two were prepared by reacting $Et_3SiSiEt_2H$ with Et_2Hg at 160° for 19 hours, and the third by reacting Et_3GeH with $EtHgSiEt_3$ at 100° for 1 to 2 hours. Many of these compounds decompose when exposed to ultraviolet light.

It therefore appears that a whole new series of compounds is beginning to develop.

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RECENT CORRELATIONS BETWEEN STRUCTURAL VARIATIONS IN A SERIES OF MOLECULES AND THEIR CHEMICAL PROPERTIES

Donald Dugre November 24, 1964

Introduction

Although relationships between structural variations in a series of molecules and their chemical properties have been known to organic chemists since 1924 (1), inorganic chemists have only recently become interested in similar correlations (2,3,4,5,6). The general form of the correlations found in the organic literature is

$$\ln \frac{k_i}{k_o} = AB \qquad \text{(I)}$$

where k_i is the equilibrium or rate constant for the process under consideration and k_o is the equilibrium or rate constant for a standard reagent undergoing the same process. The constant A is a parameter which is characteristic of the difference between the standard reagent and the reagent under consideration and B is a constant characteristic of the reaction and reaction conditions. As we shall see in the following section, this is a linear free energy relation. Probably the most familiar equation of this type is the Hammett sigma-rho relation (7). Wells (8), Jaffe (9), Taft (10), and Leffler and Grunwald (11), among others, have reviewed the multitude of variations of the Hammett equation and their applications.

Thermodynamic Effects

Consideration of equation I leads naturally to an examination of the thermodynamic effects involved in these correlations since

$$\ln K_{eq} = -\frac{\Delta F^o}{RT}$$

and

$$\ln k_{rate} = -\frac{\Delta F^{\ddagger}}{RT}$$

where ΔF^o is the change in standard free energy due to a reaction and $\Delta F^{\ddagger}$ is the free energy of activation. Then for a generalized constant K and a generalized free energy change, ΔF, the relation between a member of the reaction series and the standard for the series is

$$\ln \frac{K_i}{K_o} = \frac{\Delta F_i}{\Delta F_o} = A_i B$$

which can be rearranged to give the linear relation

$$\Delta F_i = A_i B \, \Delta F_o$$

For two members (i,j) of a reaction series, we have

$$\ln \frac{K_i}{K_j} = \frac{\ln K_i/K_o}{\ln K_j/K_o} = \frac{\Delta F_i/\Delta F_o}{\Delta F_j/\Delta F_o} = \frac{A_i B}{A_j B}$$

and

$$\Delta F_i = \frac{A_i}{A_j} \Delta F_j$$

Since the linear free energy relations (L.F.E.R.) commonly used by organic chemists contain only two parameters, the analysis up to this point has considered only the effect due to a single change from the standard compound to the compound being compared. But, since the L.F.E.R. used by inorganic chemists contain four parameters, a more general analysis is needed.

Adopting the approach of Glasstone, Laidler and Eyring (12) and Wells (8), let us consider the effect of independent variables x, y,... on the arbitrary free energy change ΔF ($\Delta F = f(x,y,\ldots)$)

$$d\Delta F = \left(\frac{\partial \Delta F}{\partial x}\right)_T dx + \left(\frac{\partial \Delta F}{\partial y}\right)_T dy + \ldots$$

or taking x_o, y_o,... as arbitrary standards for the values of the variables x,y...

$$d\Delta F = \left(\frac{\partial \Delta F}{\partial x}\right)_T (x-x_o) + \left(\frac{\partial \Delta F}{\partial y}\right)_T (y-y_o) \quad \ldots$$

$$\left(\frac{\partial \Delta F}{\partial x}\right)_T = g_x \quad \text{and} \quad \left(\frac{\partial \Delta F}{\partial y}\right)_T = g_y$$

$$d\Delta F = g_x(x-x_o) + g_y(y-y_o) \quad \ldots$$

Considering only a single term, for two reactions A and B,

$$d\Delta F_A = g_x^A(x-x_o)$$

$$d\Delta F_B = g_x^B(x-x_o)$$

$$d\Delta F_B = \frac{g_x^A}{g_x^B} d\Delta F_A$$

or

$$\ln\left(\frac{K_i}{K_o}\right)_B = \frac{g_x^A T_B}{g_x^B T_A} \ln\left(\frac{K_i}{K_o}\right)_A$$

If the temperature at which reaction A occurs (T_A) is equal to the temperature at which reaction B occurs (T_B), and reaction series A is taken as a standard, then

$$\ln \frac{K_i}{K_o} = \frac{g_x^A}{g_x^B} X_i$$

$$G_{AB} = \frac{g_x^A}{g_x^B} \qquad X_i = \ln\left(\frac{K_i}{K_o}\right)_A$$

$$\ln\left(\frac{K_i}{K_o}\right)_B = d\,\Delta F_B = G_{AB} X_i \qquad \text{(II)}$$

which is the usual two parameter correlation.

In order that the linear free energy relationship (II) exist between reaction series A and B, it is necessary that

a) the ratio $\frac{g_x^A}{g_x^B}$ remain constant over the range of variation of x.

b) the ratio $\frac{(X_i - X_o)_A}{(X_i - X_o)_B}$ remain constant

c) only one variable X be involved.

Leffler and Grunwald (11) have obtained the same results using a different analysis. They show that G_{AB} is a function only of a term added to correct for the arbitrary separation of the standard free energy of the molecule into free energies of its constituent parts. In addition, they show that for a four parameter relation (two correction terms), there can be no cross terms such as

$$\left(\frac{\partial \Delta F}{\partial x \cdot y}\right)_T$$

in the L.F.E.R. as it has been defined. Their results then require that for the case where two independent variables x and y are operating,

$$d\,\Delta F = G_x^{AB} X_i + G_y^{AB} Y_i$$

where G_y^{AB} and Y_i are defined in the same way as G_x^{AB} and X_i. Then the restrictions on the two parameter equation given above must apply to both terms simultaneously.

Since

$$\Delta F = \Delta H - T\Delta S$$

$$d\Delta F = \left(\frac{\partial \Delta H}{\partial x}\right)_T dx + \left(\frac{\partial \Delta H}{\partial y}\right)_T dy - T\left[\left(\frac{\partial \Delta S}{\partial x}\right)_T dx + \left(\frac{\partial \Delta S}{\partial y}\right)_T dy\right]$$

Then, in order that the previous restrictions a,b,c be valid, it is necessary that one of the following conditions holds for the two parameter equation:

d) $\left(\frac{\partial \Delta S}{\partial x}\right)_T = 0$ isentropic series

e) $\left(\frac{\partial \Delta H}{\partial x}\right)_T = 0$ isenthalpic series

f) $\left(\frac{\partial \Delta S}{\partial x}\right)_T = \beta\left(\frac{\partial \Delta H}{\partial x}\right)_T$ isokinetic series

Since the existence of any one of the restrictions d-f is not very probable, and since for the four-parameter LFER, it is necessary that the same restrictions be true for simultaneous variations in x and y, it is understandable that four-parameter LFER are comparatively rare.

Two Parameter Linear Enthalpy Equation

Errede (2) has found that the dissociation energy D(X-Y) of a series of diatomic molecules can be reproduced by the equation

$$D(X\text{-}Y) = Le_x e_y$$

where e_x is a parameter for X, e_y is a parameter for Y and L is characteristic of the type of bond between X and Y.

His method is to plot the bond energies D(R-X) versus the discrete variable parameter e_x which is chosen so that minimum scatter is obtained in the plots. (R = organic group, X = I, Br, Cl, H, F). The best straight lines are then chosen for each R series and the slope a, which is characteristic of the R group, is computed. He then considers molecules of the type $(R_1\text{-}R_2)$ where each R is a $CA_1A_2A_3$ group; A = (H, F, Cl, Br, I, or CX_3) where the X's are as given above. e_1 is then determined from the line for the $D(R_1\text{-}X_i)$ series and e_2 from the $D(R_2\text{-}X_i)$ series. It is found that $D(R_1\text{-}R_2) = a_1e_2 = a_2e_1$ and therefore

$$\frac{a_1}{e_1} = \frac{a_2}{e_2} = L \text{ (a constant independent of R and X)}$$

Errede is able to generate 986 new data from 49 parameters. The standard deviation is approximately 2%.

Neale (3) has found that it is possible to calculate e values for organic groups whose ionization potentials are known and for inorganic radicals whose ionization potentials (I) and electron affinities (E) are known. He separates the bonding groups into three classes:

A. groups in which unpaired electrons are localized on an atom other than carbon with non-bonded s or p electrons (primarily inorganic radicals)

$$e_A = 0.115(I_A - E_A) - 0.07$$

B. groups in which the unpaired electron is on carbon and is conjugated to an electron system ($R-C\equiv C-CH_2$., $HC\equiv C-CH_2$., etc.)

$$e_B = 0.115 I_B - 0.07$$

C. groups which do not fit into classes A or B ($R_mH_{3-m}C$., C_6H_5., $CH_2{=}CH$., H·, etc.)

$$e_C = 0.0561 I_C + 0.55$$

If we take the series R_oX as a standard and take everything relative to R_oX_o, then

$$D(R_oX) - D(R_oX_o) = (e_X - e_{X_o})Le_{R_o}$$

and for another reaction series

$$D(RX) - D(RX_o) = (e_X - e_{X_o})Le_R$$

thus

$$(20) \quad d\Delta H = D(RX) - D(R_oX) = (e_X - e_{X_o})L(e_R - e_{R_o}) = A_X B_R$$

where $A_X = e_X - e_{X_o} = y - y_o$ and $B_R = L(e_R - e_{R_o}) = \frac{d\Delta H}{dy}$

Four Parameter LFER

Edwards followed the lead of Swain and Scott (13) in attempting to find an LFER which took note of the fact that rates of displacements on alkyl carbon atoms do not follow the normal basicities of the attacking group (14,15,16). He found that many rate data for nucleophilic displacements and equilibria involving some degree of covalent bonding could be correlated by

$$\log \frac{K}{K_o} = \alpha E_n + \beta H. \qquad \text{(III)}$$

The constants α and β are dependent on the identity of the substrate and $\frac{K}{K_o}$ is a relative (to water) rate or equilibrium constant. The constant En is the nucleophilicity constant of the donor and H is the basicity of the donor relative to the basicity of a proton. The nucleophilicity constant E_n is calculated from

$$E_n = E_o + 2.60$$

where E^o is the electrode potential for oxidative dimerization of the donor and 2.60 represents the electrode potential for the oxidative dimerization of water. The relative basicity H is determined from

$$H = pKa + 1.74$$

where pKa is for the conjugate acid in aqueous solution and 1.74 is a correction for the pKa of H_3O^+.

Ideally, it should be possible to get the α's and β's for 58 substrates from 116 data and the E_n's and H's for 24 nucleophiles from 48 data and thus correlate an additional 1228 pieces of data, but because of lack of some vital numbers and in order to keep the error small, Edwards has used an unstated number of data in a least squares calculation.

In a later paper (5), Edwards redefined equation (III) in the following way:

$$E_n = aP + bH$$

$$P = \log \frac{R}{R_{H_2O}}$$

where R = molar refraction of nucleophile extrapolated to infinite wavelength and R_{H_2O}, molar refraction of water extrapolated to infinite wavelength. Thus

$$\log K/K_o = AP + BH$$

where $A = \alpha a$ and $B = \beta + b\alpha$. The immediate advantages of this redefinition are that the data for R/R_{H_2O} are easier to obtain than E_n and that commonly invoked dependence of the strength of electron donor-acceptor interactions on polarizability of the donor is explicitly given.

Analysis of Edwards' equation shows that it fits into the four parameter thermodynamic scheme given earlier, where

$$P = X_i, \quad A = G_x^{AB}, \quad H = Y_i, \quad B = G_y^{AB}.$$

Four Parameter Linear Enthalpy Relation

Wayland (6) recognized that a four parameter relation would be necessary to reproduce the observed reversal of relative heats of formation of certain Lewis acid-base combinations (17,18) (e.g., $(C_2H_5)_2O$ and $(C_2H_5)_2S$ with I_2 and C_6H_5OH). Taking Mulliken's model of binding in charge-transfer complexes (19,20,21) as a starting point, he concluded that

$$\Delta H_{AB} = I_A I_B + C_A C_B$$

where I_B is the relative dipole moment of the base, C_B is the relative polarizability (as determined from molar refraction) of the base and I_A and C_A are constants characteristic of the acid. The terms $I_A I_B$ and $C_A C_B$ correspond roughly to electrostatic interaction between the acid and base and charge transfer interaction between the acid and base respectively. Using this treatment, Wayland has been able to generate 250 additional heats of formation with 88 parameters. The standard deviation for the correlation of 20 acid-base combinations cited in his thesis is 4% which is within experimental error.

An examination of the parameters I_B and C_B for the bases and I_A and C_A for the acids shows a striking similarity with Pearson's (22), and Pearson and Edwards' (23) qualitative discussion of "hard" and "soft" acids and bases. Taking bases whose polarizability (electron donating ability) term is large relative to their dipolar (coulombic interaction) term as soft, and defining hard bases and hard and soft acids in the same way, the phenomena of hard acids interacting most strongly with hard bases and soft acids interacting most strongly with soft bases is neatly rationalized. Moreover, Pearson and Edwards' discussion of the factors underlying these phenomena are perfectly consonant with most chemists' picture of the variation in properties for the donors and acceptors considered.

Comments

It must be emphasized that none of the relationships discussed above presume to be an explanation or theory of the effect of structural changes on chemical properties. Their primary value at present is that they summarize a large number of data in a way that makes the trend in change of properties due to structural variations apparent. DeWar and Grisdale (24,25), Jaffe (26), and Sager and Ritchie (27) have attempted to give an explicit treatment (by molecular orbital theory) of the trends summarized by the Hammett equation, but they have not succeeded. Grunwald (28), Dewar (29), Sager and Ritchie (30) and Ehrenson (31) have recently discussed the problem of physical interpretation of LFER and similar relations.

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SOME TRAPPED RADICAL STUDIES

Michael Garrett December 15, 1964

INTRODUCTION

In recent years, the technique of stabilization of free radicals through matirx isolation has been increasingly used in the identification and structural determination of these species. A book (1) and several short review articles (2, 3, 4, 5) have been written on various aspects of radical trapping.

The great advantages of matrix isolation are (1) the fact that a high concentration of radicals is present in the system for a long time, enabling spectroscopic techniques to be used (especially I-R) that could not be applied to gas or liquid phase problems and (2) the wide flexibility possible in generation of the species of interest.

Inert gas matrices are typically prepared by condensing the gaseous reactive or reactant species with a large excess of the inert gas onto a cold surface. The latter is usually maintained at 4°-20°K. in order to prevent destruction of the radicals by diffusion through the lattice. Radicals may be generated in the gas phase prior to condensation by electrical or microwave discharges or high temperature ovens. The species of interest may be produced in situ by the decomposition of a trapped precursor. Methods used include photolysis, x-ray and electron bombardment. However, recombination due to the Brank-Rabinowitsch "cage effect" imposes limitations on the in situ production of radicals (see examples discussed below).

Matrix materials are not limited to simple gases; hydrocarbon and other organic glasses, formed by rapid condensation of the corresponding liquids, have been used for large organic radicals and ions (1), and radicals have been trapped in certain ionic crystals (4).

Once the radical has been trapped, it can be studied at leisure by methods which include I-R, optical and E.S.R. spectroscopy. Perturlations from "matrix effects" may be large and may cause splitting of the features, especially in optical spectroscopy. The analysis of such spectra is difficult, and even identification of the species may not be possible without outside information. Where gas phase spectra have been recorded, correlations with matrix bands are possible, but care must be exercised to distinguish "hot bands" which would not be expected to occur in matrix spectra because of the low temperature. Isotope shifts in I-R bands also provide useful information. Structural data is somewhat limited by the fact that, with the exception of a few hydride molecules, rotational five structure is not observed in matrix spectra.

Attempts to explain the peculiarities of matrix spectra have met with mixed success. There is evidence of multiple trapping sites from E.S.R. studies of trapped H and alkali metal atoms in rare gas matrices (6, 7). The occurrence of satellite bands in electronic spectra of matrix isolated species has also been explained in terms of multiple sites (24). Most attempts to account for shifts in band

positions, especially in I-R spectra, are based on van der Waal's forces and exchange-repulsion (Pauli exclusion principle) forces (4, 5, 8, 9) (cf - "A Discussion of the Effect of Environment upon Molecular Energy Levels", Proc. Roy. Soc., A255, 1-81 (1960)). Aggregation, which can become important at the relatively high concentrations used in I-R work, and the far from perfect crystalline nature of most matrix deposits increase the complexity of the problem (1, 10, 33).

SOME RECENT EXAMPLES OF MATRIX ISOLATION OF FREE RADICALS.

HCO, DCO (11)

First triatomic, matrix-isolated radicals to be detected by I-R spectroscopy, these molecules were produced by photolysis of HI or HBr and DI or DBr in a CO matrix at 20°K. The optical spectrum was also recorded and results correlated with gas-phase measurements as a check in the identification of the species. This example differs from most in that the matrix itself is a reactant, a technique which the authors felt was "... an effective way of circumventing the inhibition of photolysis by the cage effect...."

HO_2 (12)

Another approach to the problem of recombination of radicals produced within the same trapping site is illustrated by work involving the elusive species HO_2, which was produced by photolysis of HI or HBr and O_2 mixtures in an Ar matrix at 4°K. The H atoms arising from photolysis are sufficiently mobile to diffuse through the matrix and react with the O_2. The use of DI, O^{18} (100%) and O^{18}-O^{16} mixtures confirmed the assignment of the observed I-R peaks to HO_2.

KrF_2 (13)

Peaks appearing in the I-R spectra of an F_2-Kr-Ar (1:70:220) mixture after photolysis at 20°K. were assigned to the molecule KrF_2. XeF_2 was also prepared by the same method for comparison. No change was observed when F_2 and Ar were photolyzed alone.

HOCN, DOCN (14)

These molecules were formed in situ upon photolysis at 4°K. or 20°K. of their stable tautomers HNCO and DNCO in an Ar or N_2 matrix. Determination of the structure of the absorber was by means of I-R spectra. For the mechanism of the rearrangement, which is of some interest, two mechanisms have been proposed:

(1) HNCO + → NCO + H → HOCN

(2) HNCO + → NH + CO → CO → HOCN
NH

The second route is favored because the mobility of the H atom should lead to the formation of NCO, which was not observed after prolonged photolysis.

CF_2 (15, 16)

A third useful technique for the in situ production of trapped radicals involves the decomposition into the radical of interest plus a species of "special stability", so that recombination is inhibited. An example is the recent work on the photolysis of CF_2N_2 in Ar and N_2 matrices, which leads to the production of $CF_2 + N_2$. Optical and I-R spectra were taken, and from the C^{13} (natural abundance) stretching frequency shifts a bond angle of 108° was estimated. Identification was made by correlation of matrix and gas-phase optical spectra. C_2F_4 forms if diffusion is allowed to occur.

NH (1, 17)

This molecule has been studied repeatedly since it was first proposed to arise from the pyrolysis of HN_3. The most recent effort was directed towards establishing a mechanism for the photolysis of HN_3 in solid matrices. Photolysés were carried out at 4°, ~14°, and 20°K. in Ar, N_2 and CO matrices. Identification was accomplished by the I-R and optical spectra and by the use of DN_3 and $HN^{15}N_2{}^{14}$. Photolysis of HN_3 is known to occur by cleavage of the HN...N_2 bond, but some evidence was formed for the cleavage of the H--N_3 bond as well. In the CO matrix, a high concentration of HCO in addition to HNCO was observed. Since HNCO and NH were not observed to undergo photolysis themselves, the H atoms which reacted to form HCO probably came directly from HN_3.

NF, NCl, NBr, (18)

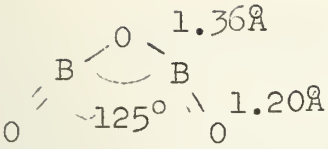
These species were produced in Ar or N_2 matrices at 4° or 20°K. by photolysis in situ of the corresponding halogen azide. Assignments were made for the I-R peaks of the parent FN_3, ClN_3 and BrN_3 molecules as well as for the product HX. The correctness of these assignments was checked by the use of FN^{15}-$N_2{}^{14}$, and by the correspondence of the NBr frequency to that formed in gas phase spectra.

$HBCl_2$, $DBCl_2$ (19)

Mixtures of BCl_3-$HBCl_2$ and the deuterated species were trapped in Ar at ~10°K. in order to study conveniently their I-R spectra. Gas phase work is hampered by the disproportionation $6HBCl_2 \rightleftarrows 4BCl_3 + B_3H_6$. Frequencies observed were compared to gase phase and calculated ones.

B_2O_3 and B_2O_2 (20)

These two species were trapped by condensing vapor effusing from an induction heated molybdenum knudsen cell with an excess of Ar or Xe. From the known vapor pressure of B_2O_3 and the orfice geometry, it was possible to calculate concentrations in the matrix. The I-R spectrum of B_2O_3 was analyzed in detail, using both natural boron(81.6% B^{11}, 18.4% B^{10}) and 100% B^{10}. The V structure proposed on the basis of electron diffraction results was confirmed.



For $B_2{}^{10}O_2$, which was formed by heating $B_2{}^{10}O_3$ with excess B^{10}, only one band was observed and a correlation was made to gas-phase emission I-R spectra. The molecule is apparently linear.

C_2, C_3, C_n

C_2 has been identified by Robinson and McCarty from its electronic absorption spectrum in matrices formed by condensing the products of a discharge through hydrocarbon vapor-rare gas mixtures (21). They observed only transitions from the $^3\Pi_u$ state and concluded that this is the ground state of the molecule. However, Ramsay and Ballik (22) found $^1\Sigma_g^+$ to be the ground state in the gas phase, and Ramsay noted that the metastability of $^3\Pi_u$ re : $^1\Sigma_g$ may have prevented the observation of the latter in the matrix (1). Later, Schoen, who produced C_2 by electron bombardment of trapped hydrocarbonds, observed some electronic transitions which he designated as originating from the $^1\Sigma_g$ state (23). These results were partially corroborated by Weltner (24), who observed C_2 bands after diffusion was allowed to occur in matrices containing C_3.

The latter species is a major constituent of carbon vapor (as determined mass-spectrometrically) and was trapped from high temperature vapor emitted from a carbon containing resistance heated Ta oven or from an induction heated carbon block (24, 25). Identification of C_3 in the matrix was accomplished by I-R spectra and by electronic spectra in absorption and in flourescence. Bands in the 4050Å region arising from a $^1\Sigma \rightarrow {}^1\Pi$ transition were correlated with recent gas phase measurements by Herzberg et.al. (26).

The very low value of $V_2{}^{11} \simeq 70\ cm^{-1}$ calculated by Dixon (27) was verified (with reservations) and values for v_1'', v_3'', v_1', and v_2' were given. A long lived emission observed at 5900 Å was taken to be $^3\Pi_v \rightarrow {}^1\Sigma_g^+$.

Upon warm up, I-R bands appeared which were assigned to linear C_n species as discussed theoretically by Pitzer and Clementi (28).

Si_2, Si_3, Si_4 (29)

These species have been observed in Si vapor by mass spectrometry and were trapped in a similar way to C_3. Si_2 was definitely identified by a correlation of the absorption spectrum to that observed in the gas phase (30, 31), and the ground state was shown to be $^3\Sigma_g^-$. Another series of bands, involving only one vibrational frequency (V_1') were assigned to Si_3, but this is tentative. A weaker series of bands is thought to be due to Si_4.

SiC_2, Si_2C, Si_2C_3 (29)

These species were observed in matrices prepared by trapping the vaporization products of SiC.

Absorption bands due to SiC_2 were easily distinguished by correlations to gas phase spectra. Features missing in the matrix spectra were assumed to be "hot bands" and the analysis was corrected. I-R and emission spectra were also recorded. SiC_2 is linear and asymmetric and has a $^1\Sigma$ ground state similar to C_3.

Two band systems at ~5300Å and ~4900Å were tentatively assigned to Si_2C and another system to the species Si_2C_3. The latter molecule has been observed mass spectrometrically; evidence for its presence in the matrix is based upon the appearance of a progression with the characteristic stretching frequency of C_3. The complexity of the I-R spectrum and the large number of progressions in the optical spectrum indicate that this molecule is the unsymmetrical $SiSiC_3$.

The electronic configuration of these species was discussed in terms of Walsh's theory (32).

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MICROPOTENTIOMETRIC STUDY OF CHLORIDE BINDING TO MOYOGLOBIN

Hassan Tayim March 9, 1965

Introduction

The effects of binding of small ions by protein molecules in solution have been manifested as anomalous results in some physico-chemical studies of the proteins in solution[1,2,3]. It has thus become essential to understand the nature and extent of such interactions. The present work deals with the detection and evaluation of the binding of chloride ions to sperm whale ferrimyoglobin in aqueous solution of potassium chloride and myoglobin.

The method applied is based on the reduction in the thermodynamic activity of the combining chloride ions in presence of protein in solution as determined by measurement of the free ion concentration by electromotive force method.

Although the e.m.f. method was applied to the investigation of reactions of proteins with acids and bases as early as 1898[4], the binding by proteins of anions other than hydroxyl ions was first demonstrated by e.m.f. methods in 1932 by Hitchcock[5]. The first quantitative study of this sort, however, was made by Scatchard and co-workers (1950)[6,7].

Theoretical:

(a) E.m.f. of Concentration Cell:

A concentration cell comprising two Ag/AgCl electrodes immersed in potassium chloride solutions of equal concentration (activity) has a zero e.m.f. If myoglobin solution is added to one of the two electrode compartments, the cell may develop an e.m.f. depending on the extent of chloride ion binding to myoglobin and on the effect of myoglobin on the liquid junction potential (Ej).

It can be shown that the e.m.f. of such a cell is given by

$$E = (RT/F)\ln(a_2/a_1) + Ej \quad (1)$$

with the electrode in the solution of lower activity being positive with respect to the other electrode, if Ej is zero or has the same polarity. For dilute solutions of protein equation (1) can be written as[6]

$$E = (RT/F)\ln(c_2/c_1) + Ej \quad (2)$$

(b) Theory of Anion Binding to Proteins:

Tanford[8] and Klotz[9] have shown that there are three general cases encountered in the treatment of the theory of binding:

(i) For the simplest case where there are n identical independent (non interacting) sites on the protein molecule with n identical equilibrium constants, the average number of anions associated with each protein molecule ($\bar{v}$) can be given from laws of chemical equilibria by

$$\bar{v}/(n-\bar{v}) = kc \quad \_ \_ \_ \qquad (3)$$

where k is the overall association constant, c the concentration of free (unbound) chloride.

(ii) When there are n identical sites, but binding at any one site affects the binding affinity at other sites, the average binding is given by

$$(\bar{v}/cf)\exp(2w\bar{v}) = K(n-\bar{v}) \quad \_ \_ \_ \qquad (4)$$

K being an intrinsic association constant and w the electrostatic interaction factor.

(iii) In the more complicated case where there are different classes of binding sites, if n_1 sites have intrinsic association constant $K^{(1)}$, n_2 sites have constant $K^{(2)}$, etc.--. in the absence of interaction between sites v is given by

$$\bar{v} = \frac{n_1K^{(1)}c}{1 + K^{(1)}c} + \frac{n_2K^{(2)}c}{1 + K^{(2)}c} + \text{-----} \qquad (5)$$

and if there is interaction between sites, v is given by

$$\bar{v} = \frac{n_1K^{(1)}c\ \exp(2w\bar{v})}{1 + K^{(1)}c\ \exp(2w\bar{v})} + \frac{n_2K^{(2)}c\ \exp(2w\bar{v})}{1 + K^{(2)}c\ \exp(2w\bar{v})} \qquad (6)$$

Experimental:

(a) Electrodes: Ag/AgCl electrodes were prepared by electrolytically depositing silver on clean platinum electrodes from potassium silver cyanide solution, then partially chloridizing the silver layer by electrolytic oxidation in hydrochloric acid.

(b) Concentration Cells:

A Y shaped cell was used after Scatchard[6,7], with saturated potassium chloride bridge, especially in the work on serum albumin. A capillary junction cell, which is a modification of a cell used by Smith and Speakman[10] and Dunsmore and Speaksman[11] was used in the major part of the work. The

contact between the two solutions in the electrode compartments was produced at the end of a capillary tube. The junction was reproducible and caused no serious diffusion problems.

(c) Potentiometer-Electrometer Setup:

A highly sensitive K3 micropotentiometer (Leeds and Northorp) was used in conjunction with a locally designed and constructed vibrating reed electrometer.

Results

The following observations were made:

(1) The addition of myoglobin to chloride solution produced an e.m.f. in the opposite direction expected on basis of chloride binding to myoglobin. The e.m.f. increased with decreasing the pH of the system as expected by theoretical considerations.

(2) Repeating the experiment of Scatchard[6] under experimental conditions almost identical to his, we arrived to the conclusion that the signs of the e.m.f.'s as reported by Scatchard and co-workers were actually reversed.

(3) E.m.f. was measured for myoglobin + chloride/chloride system under conditions of minimum or nc binding[12]. The results indicated that myoglobin (aside from binding) produces an e.m.f. of a sign opposite to the e.m.f. produced by binding. The latter could be calculated by applying a correction for the "liquid junction potential".

(4) Myoglobin binds chloride ions at at least 20 sites as shown in the following table

Myoglobin concentration	Isoinic pH	Chloride Binding Sites and their Constants					
		n_1	(k_1)	n_2	(k_2)	n_3	(k_3)
moles/l							
0.001	6.47	1	(15,000)	6	(100)	13	(10)
0.0001	6.25	1	(50,000)	6	(5,000)	13	(20)

Discussion

The results obtained can be correlated with the known structure of myoglobin: it is known from the work of Edmundson and Hirs[3] that the cationic groups on the myoglobin molecule include

4 arginines, 12 hestidines and 19 lysines. It is also known from the work of Breslow and Gurd[13] that 6 of the hestidine groups are masked or inaccessible to interacting ions. The technique applied in the present work excludes the counting of the 4 arginines (normal pK greater than 12)[14]. Hence the 6 binding sites of intermediate binding affinity could be assigned to the 6 hestidine imidazolium groups, the 13 sites of weaker affinity to lysine amine groups, and the single site of the highest binding affinity to a special binding site on the myoglobin molecule. It has been actually reported by Stryer, Kendrew and Watson[15] that such a special site does exist.

In view of its structural similarity to myoglobin, hemoglobin posed an interesting case. A few measurements carried out in the course of the present investigation indicated, however, that it binds chloride ions to a much lesser extent than myoglobin. This may suggest that most of the cationic groups on the hemoglobin molecule are either of very weak binding affinity or inaccessible to interacting chloride ions.

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[illegible]

(1) [illegible]

(2) [illegible]

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(12) [illegible]

(13) [illegible]

(14) [illegible]

(15) [illegible]

(16) [illegible]

ALKYNE-BRIDGED TRANSITION METAL COMPLEXES

R. E. Wagner April 13, 1965

Introduction

Since their discovery (1) these complexes have evoked many interesting questions. Their characterization presents a study of the application of spectral data and chemical reactions. These complexes are used as antiknocks in fuels (2), as starting materials in the preparation of other organometallic complexes (3, 4), and as catalysts in the cyclic trimerization of alkynes (5, 6).

Dinuclear Complexes

The dinuclear complexes containing one mono-alkyne molecule are summarized by the following generalized formulas.

I.	$(CO)_3M(R\text{-}C_2\text{-}R^1)M(CO)_3$	M = Co
II.	$LM(R\text{-}C_2\text{-}R^1)ML$	M = Ni; L = ligand containing cyclopentadienyl moeity
III.	$M_2L_2(CO)_4(R\text{-}C_2\text{-}R^1)$	M = Mo; L = cyclopentadienyl ion or tetraphenylcyclobutadiene

R and R^1 may be the same or different and may encompass a wide range of groups. (Table 1) The type of R-groups affects the physical and chemical properties and the method of preparation.

Physical Properties

The complexes are intensely colored solids or oily liquids. The solids are readily sublimable. The complex $Co_2(CO)_6(F_3C\text{-}C_2\text{-}CF_3)$ sublimes at room temperature and atmospheric pressure. (7, 8) The substituents of the alkyne play an important role in determining the sensitivity to air oxidation. Tilney-Bassett (9) notes that for complexes of type II those derived from phenyl-substituted acetylenes are stable as solids, while those derived from alkyl-substituted acetylenes are slowly decomposed. Only the complexes derived from perfluoro-2-butyne are stable in nonpolar solvents. (8)

Preparation

The most common preparation of the cobalt complexes uses dicobalt

octacarbonyl and the appropriate acetylene. (1, 4, 8)

[1] $Co_2(CO)_8 + R\text{-}C_2\text{-}R^1 \rightarrow (CO)_3Co(R\text{-}C_2\text{-}R^1)Co(CO)_3$

Under certain conditions, this reaction is quantatative. (1) Hübel noted that the products obtained depend on the temperature and on the substituents of the acetylenic molecule. (4) Kinetic studies have suggested a reactive form of $Co_2(CO)_8$. (10, 22) There is no large variation in reaction rate with alkyl substituents (R, R^1). (11) A less favorable preparation is.(4, 12, 21)

[2] $[Co(CO)_4]_2Hg + R\text{-}C_2\text{-}R^1 \rightarrow (CO)_3Co(R\text{-}C_2\text{-}R^1)Co(CO)_3$+ other products

Complexes of type II are prepared by the following reactions. (9, 8, 2, 37)

[3] $CpNi(CO)_2NiCp + R\text{-}C_2\text{-}R^1 \rightarrow CpNi(R\text{-}C_2\text{-}R^1)NiCp$

[4] $Cp_2Ni + R\text{-}C_2\text{-}R^1 \rightarrow CpNi(R\text{-}C_2\text{-}R^1)NiCp$

Dubeck (13) has shown that, when one or both of the R-groups is electron-withdrawing, the corresponding complex can be prepared by a replacement reaction.

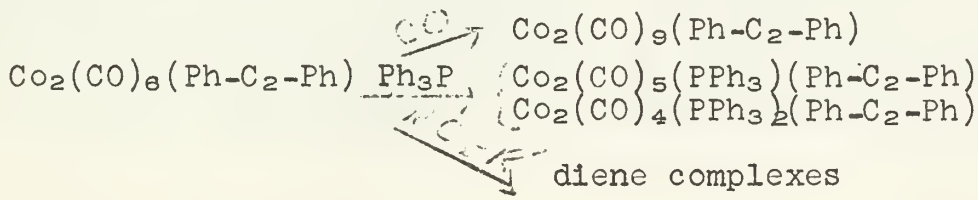
[5] $CpNi(Q\text{-}C_2\text{-}Q^1)NiCp + Q\text{-}C_2\text{-}Q^1 \rightleftarrows CpNi([\text{-}C_2\text{-}Q^1)NiCp + R\text{-}C_2\text{-}R^1$

Attempts to prepare these complexes by 3. or 4. have either failed (9) or yielded complexes $(Q\text{-}C_2\text{-}Q^1)NiCp_2$. (14, 37)

The iron complexes $Fe_2(CO)_6(R\text{-}C_2\text{-}R^1)$ were considered to be analogous. (15, 16) A recent structure determination has disproved this assumption. (32, 33, 36) However, recent attempts to isolate less stable complexes have yielded complexes $Fe_2(CO)_7(R\text{-}C_2\text{-}R^1)$ which correspond formally to substitution products of $Fe_2(CO)_9$. (34) The molybdenum complexes are the first reported examples of alkyne-bridged complexes containing other than a Group VIII transition metal. (17, 18, 19)

Chemical Reactions

The complex $Co_2(CO)_6(Ph\text{-}C_2\text{-}Ph)$ undergoes exchange with labeled CO at a much slower rate than its parent complex $Co_2(CO)_8$. (20) Similarly a reduced reactivity to substitution by $P(Ph)_3$ has been noted. (21) Some reactions are shown below. (21, 4, 3, 23, 24)



$$Co_2(CO)_6(R\text{-}C_2\text{-}H) \xrightarrow{H^+} Co_3(CO)_9(R\text{-}C_2\text{-}H)H$$

$$CpNi(Ph\text{-}C_2\text{-}Ph)NiCp \xrightarrow{CO} Ph\text{-}C_2\text{-}Ph + Ni(CO)_4$$

$$CpNi(Ph\text{-}C_2\text{-}Ph)NiCp \xrightarrow{NO} CpNiNO$$

Structure

Degradative reactions have proven the existence of the unpolymerized "acetylenic" molecule in these complexes. However, the results do not unambiguously indicate the nature of the "acetylenic" bond. Much of the infrared data has been interpreted to indicate the double-bond character of the C-C bond and the absence of bridging CO-groups. (1, 4, 18) A crystal structure determination of $Co_2(CO)_6(Ph\text{-}C_2\text{-}Ph)$ has shown the molecular skeleton to be as follows. (25)

A recent structure determination of the complex $Co_2(CO)_6(C_6F_6)$ shows a similar arrangement. (38)

With the exception of the complexes derived from fluorinated acetylenes (7, 8, 38), no significant shifts of the terminal CO-stretching vibrations have been noted. (1, 4, 26) Early work suggested that the number of CO-stretching vibrations could be correlated with the local symmetry (27) of the metal carbonyl fragments. Recent work by Bor (28), however, has suggested that the symmetry of the molecular skeleton is the determinant.

Bonding

The bonding has been formally described by the Inert Gas rule. The alkyne molecule is considered a four-electron donor. Metal-metal bonding is postulated to account for the observed diamagnetism. The complexes $Fe_2(CO)_6(R\text{-}C_2\text{-}R^1)$ give an insight into the applicability of this rule. The structural parameters of the complex $Co_2(CO)_6(Ph\text{-}C_2\text{-}Ph)$ do not unambiguously lead to an assignment of metal hybridization. (25, 29) The C-C bond distance makes a tetrahedral hybridization of the carbons seem unlikely. An approximate molecular orbital calculation based on a trigonal bipyramidal hybridization of the metal orbitals has been done. (29)

Trinuclear Complexes

The trinuclear complexes which have been reported are listed in Table II. (15, 16, 30, 34) Their characterization has been scanty. The complexes are diamagnetic. Degradative reactions suggest that an unpolymerized "acetylenic" molecule is present. Recent attempts to isolate less stable complexes have yielded $Fe_3(CO)_8(Ph\text{-}C_2\text{-}Ph)$. (34) A recent structural determination has indicated that in one of the isomers of $Fe_3(CO)_8(Ph\text{-}C_2\text{-}Ph)$ (16, 34), unpolymerized "acetylenic" molecules are acting as both π^- and σ^- donors. (34, 35)

Tetranuclear Complexes

Tetranuclear complexes are of two types. In the first type, both triple bonds of a diyno molecule act as bridges (1, 6, 9, 30) Based on their diamagnetism, infrared spectra, and method of preparation, structures analogous to those of the dinuclear complexes have been proposed. These complexes are prepared by reactions 6 and 7.

[6] $Cp_2Ni_2(Ph\text{-}C_2\text{-}C_2\text{-}R) + M_a(CO)_n \rightarrow (CpNi)_2(Ph\text{-}C_2\text{-}C_2\text{-}R)M_2(CO)_6$

$R = Ph, H;\ M_a(CO)_n = Co_2(CO)_8$ or $Fe_3(CO)_{12}$

[7] $Co_2(CO)_8 + (R\text{-}C_2\text{-}(CH_2)\text{-}C_2\text{-}R^1) \rightarrow Co_2(CO)_6(R\text{-}C_2\text{-}(CH_3)_n\text{-}C_2\text{-}R^1)Co_2(CO)_6$

The second type of tetranuclear complex contains one mono-alkyne molecule per molecule of complex. (30, 4) The cobalt complexes have been prepared in a manner formally analogous to the preparation of the dinuclear complexes. (4)

[8] $Co_4(CO)_{12} + R\text{-}C_2\text{-}R^1 \rightarrow Co_4(CO)_{10}(R\text{-}C_2\text{-}R^1)$

Two structures for the complex $Co_4(CO)_{10}(Ph\text{-}C_2\text{-}PH)$ have been proposed based on conflicting infrared spectra. (30, 4) A recent structural determination of the complex $Co_4(CO)_{10}(E\text{-}C_2\text{-}E)$ has shown a distorted tetrahedral arrangement of the cobalt atoms. (39)

Hexanuclear Complexes

Two hexanuclear complexes derived from 1,3,5-triethynylbenzene and 1,2,4-triethynylbenzene have been prepared. (6) The bonding in these complexes is believed to be similar to that in the dinuclear complexes.

Dinuclear Complexes

Table I

Type I	$Co_2(CO)_6(R\text{-}C_2\text{-}R^1)$	Reaction	Reference
alkyne	m.p. °C		
phenylacetylene	(liq.)	1	(1)
isopropenylacetylene	31.8-32.8[a]	1	"
propargyl alcohol	52.2-52.6[a]	1	"
phenylpropiolic acid	120[b]	1	"
trimethylsilyl phenylacetylene	64	2	(4)
acetylene	13.0-13.6[a]	1	(1)
cyclodecyne	(liq.)	1	"
diphenylacetylene	109.5-110.0[a]	1	"
perfluoro-2-butyne	114	1	(7,8)
diphenylbutadiyne	57-59	1	(6)
"perfluorocyclohex-1-yn-3ene"	47-48	-	(38
Type II	$(CpNi)_2(R\text{-}C_2\text{-}R^1)$		
Acetylene	143-44	3,4	(2,9)
2-butyne	55	3,4	(2,9)
perfluoro-2-butyne	91-93	3,4	(2,937)
diphenylbutadiyne	121	3	(9)
diphenylacetylene	149-150	3	(9)
phenylacetylene	132-33	3	(9)
Type III	$Cp_2Mo_2(CO)_4(R\text{-}C_2\text{-}R^1)$		
L = cyclopentadienyl ion			
diphenylacetylene	239-40	--	(17,18)
phenylacetylene	138-39	--	(17,18)
[L ≡ tetraphenylcyclobutadiene			
diphenylacetylene	200-205[b]	--	-(19)

a corrected

b melts with decomposition

Polynuclear Complexes

Table II

Trinuclear Complexes	m.p. °C	Reaction	Reference
$(CpNi)_2(Ph\text{-}C_2\text{-}Ph)Fe(CO)_3$	198-99	-	(30)
$(CpNi)_2(Ph\text{-}C_2\text{-}H)Fe(CO)_3$	121	-	(30
$Fe_3(CO)_{10}(Ph\text{-}C_2\text{-}Me)$	-	-	(15)
$Fe_3(CO)_9(Ph\text{-}C_2\text{-}Ph)$	—	—	(34)
$Fe_3(CO)_8(Ph\text{-}C_2\text{-}Ph)_2$	160[a]	-	(16,34)
Tetranuclear Complexes			
$(CpNi)_2(Ph\text{-}C_2\text{-}Ph)Fe_2(CO)_6$	180[a]	-	(30)
$(CpNi)_2(Ph\text{-}C_2\text{-}H)Fe_2(CO)_6$	168[a]	-	(30)
$Co_4(CO)_{10}(Ph\text{-}C_2\text{-}Ph)$	175-80[b]	8	(4)
$Co_4(CO)_{10}(Et\text{-}C_2\text{-}Et)$	160[b]	8	(4)
$Co_4(CO)_{10}(Ph\text{-}C_2\text{-}CO_2\text{-}Me)$	145[b]	8	(4)
$Co_4(CO)_{12}(Cl\text{-}C_2\text{-}(CH_2)_6\text{-}C_2\text{-}Cl)$	68-69	1	(1)
$(CpNi)_4(Ph\text{-}C_2\text{-}C_2\text{-}Ph)$	296-97	3	(9)
$(CpNi)_2(Ph\text{-}C_2\text{-}C_2\text{-}Ph)Co_2(CO)_6$	------	6	(9)
$(CpNi)_2(Ph\text{-}C_2\text{-}C_2\text{-}Ph)Fe_2(CO)_6$	156	6	(9)
$[Co_2(CO)_6]_2(Ph\text{-}C_2\text{-}C_2\text{-}Ph)$	117-120[b]	7	(5)
Hexanuclear Complexes			
$[Co_2(CO)_6]_3L$	127-28[b]	-	(6)
L≡ 1,3,5-triethynylbenzene			
$[Co_2(CO)_6]_3L^1$	120-130[b]	-	(6)
L^1≡ 1,2,4-triethynylbenzene			

a melts with decomposition

b decomposes

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The Transition-Metal Carbonyl Hydrides and Derivatives

Anton Schreiner April 27, 1965

A. Introduction

Numerous transition-metal carbonyl hydrides have been synthesized. In general, however, their properties have been incompletely characterized. It is attempted here to provide some insight into this area of chemistry.

B. Representative Synthetic Methods and Properties

1. Syntheses

There are four important preparative methods. The guiding principle of each is to retain the metal in a low oxidation state.

a. Direct Synthesis. The metal, one of its salts or a complex of the metal reacts with CO and H_2 under pressure and at elevated temperature. The following reactions are of this direct type:

$$Co + CO + H_2 \xrightarrow{280\text{ atm},\ 180^\circ} H\,Co(CO)_4 \qquad (11)$$

$$Cr(C_5H_5)_2 + CO + H_2 \xrightarrow{\Delta,\ P} (C_5H_5)Cr(CO)_3H \qquad (4)$$

$$Rh\,Cl_3 + CO + H_2 \xrightarrow{200\text{ atm},\ 200^\circ} H\,Rh(CO)_4 \qquad (12)$$

$$Mn_2(CO)_{10} + CO + H_2 \xrightarrow{140\text{ atm},\ 170^\circ} H\,Mn(CO)_5 \qquad (13)$$

b. Acidification of the Alkali Salts. In this series of reactions usually the metal carbonyl or a substituted metal carbonyl reacts with a solution of an alkali metal in liquid NH_3 (14) or Na/Hg in THF (5). The resulting sodium salt is then acidified to convert it to the hydride. Examples follow:

$$Co_2(CO)_8 \xrightarrow[2)\,H^+]{1)\,Na/NH_3 \text{ or } Na/THF} H\,Co(CO)_4 \qquad (11)$$

$$Mo(CO)_6 \xrightarrow[2)\,H^+]{1)\,NaC_5H_5/THF} (C_5H_5)Mo(CO)_3H \qquad (5)$$

$$[Co(CO)_3PPh_3]_2 \xrightarrow[2)\,H^+]{1)\,Na/Hg,\ THF} [HCo(CO)_3PPh_3] \qquad (15)$$

$$Ni(CO)_4 \xrightarrow{Na/NH_3} H_2Ni_2(CO)_6 \qquad (16)$$

c. Reduction with Hydrogenating Agents (11). Two reducing agents have been employed successfully, i.e., $NaBH_4$ and $LiAlH_4$. For example,

$$[(C_5H_5)Fe(CO)_3][BPh_4] \xrightarrow{NaBH_4} [(C_5H_5)Fe(CO)_2H] \quad (18)$$

$$[(C_5H_5)Ru(CO)_2I] \xrightarrow{NaBH_4\ THF} [(C_5H_5)Ru(CO)_2H] \quad (19)$$

d. Reactions of Complexes with KOH Alcohol. Ligands CO and H are considered as originating from the alcohol (20,21). The following reactions illustrate this method

$$[Ru_2Cl_3(PEt_2Ph)_6]Cl \xrightarrow{KOH/EtOH,\ H_2O} [HRuCl(CO)(PEt_2Ph_3] \quad (22,23)$$

$$[Ru_2Cl_3(PEt_2Ph)_6]Cl \xrightarrow[\text{2-diethylaminoethanol}]{\text{LiBr in}} [HRuBr(CO)(PEt_2Ph)_3] \quad (23)$$

$$[NH_4][OsBr_6] \xrightarrow{PPh_3/C_2H_5OH} [HOsBr(CO)(PPh_3)_2] \quad (20)$$

The fact that about 80 of these reactions have been observed to occur prompts the warning that alcohols often react more vigorously than is usually suspected (20). The above four methods have been responsible for obtaining most of the compounds of Table I.

2. Some Properties and Reactions

The compounds have been obtained as liquids, solids and gases. Some are only solution species (25). Table II presents melting points and colors of several compounds. Thermal stability ranges from below -70°C to above 100°C, i.e., $H_2Fe(CO)_4$ decomposes above -70°C, while $HRe(CO)_5$ is a stable solid up to 100°C.

The acid properties of several species have been investigated. For example, the two acid constants of $H_2Fe(CO)_4$ are $K_1 \cong 3.6 \times 10^{-5}$ and $K_2 \cong 1 \times 10^{-14}$ at 0°C (26). On the other hand, the aqueous solution of $HMn(CO)_5$ is nearly neutral.

The reducing property (27) of these compounds makes them generally unstable towards air, whether in solution or in their natural state. Exceptions exist, as several carbonyl hydrides of osmium have shown very unusual oxidative and thermal stabilities. However, it is to be noted that they contain stabilizing substituted arsenes or phosphines in the Os coordination sphere (20).

The compounds or their sodium salts are also of use as intermediates for syntheses of organometallic compounds and

others. The following reactions demonstrate this behavior:

$$H_2Ni_2(CO)_6 \cdot 4NH_3 \xrightarrow{KCN/\ NH_3} [Ni(CO)_3CN]^- \quad (10)$$

$$H_2Ni_2(CO)_6 \cdot 4NH_3 \xrightarrow{PPh_3/\ NH_3} [Ni(CO)_2(PPh)_2] \quad (10)$$

$$HMn(CO)_5 \xrightarrow{GeH_4/\ THF} H_2Ge[Mn(CO)_5]_2 \quad (28)$$

$$[(C_5H_5)Mo(CO)_3H] \xrightarrow{CH_2N_2} [(C_5H_5)Mo(CO)_3(CH_3)] \quad (29)$$

It may be concluded that the chemical behavior of these compounds have not been investigated thoroughly. Their instability is probably the most important single reason.

C. Structures and Aspects of Bonding

1. Diffraction and Other Data on Bond Lengths. The Hatom has been directly located by diffraction in only one compound, $[HRh(CO)(PPh_3)_3]$. The analogous Ir complex is isostructural with it, as concluded from its powder diffraction pattern (30). In fact, a total of only four carbonyl hydrides have been investigated by single crystal x-ray diffraction, i.e., $[HMn(CO)_5]$, $[HOs(CO)Br(PPh_3)_3]$, $[(C_5H_5)_2Mo_2H(PMe_2)(CO)_4]$ and the above $[HRh(CO)(PPh_3)_3]$. Their structures appear below.

A rather interesting bond has been proposed by Doedens and Dahl in $[(C_5H_5)_2MoH(PMe_2)(CO)_4]$. These workers propose (34) a "symmetrical, localized, bent three-center metal-hydrogen-metal bond". Similar bonding occurs in $[HMn_2(PPh_2)(CO)_8]$ and $[(C_5H_5)_2Fe_2H(PR_2)(CO)_2]$, these authors claim.

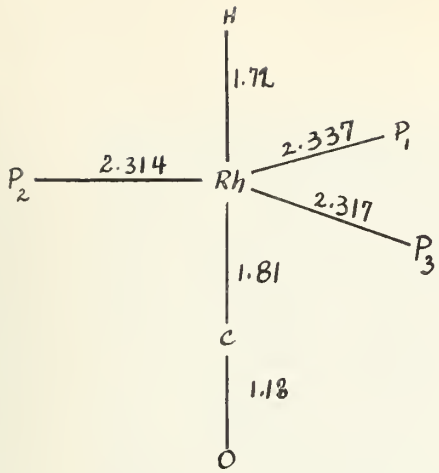
Electron diffraction studies of $H_2Fe(CO)_4$ and $HCo(CO)_4$ only show that the CO groups are tetrahedrally disposed with respect to the metal (resolution low) (35).

Semi-empirical LCAO-MO calculations (45,49) on $HCo(CO)_4$, the symmetry of which will be discussed below, place the H atom ca. 1.2A from the Co (49).

In one study broad-line NMR (37) was used to obtain the H-H interatomic distance (1.88A) in $H_2Fe(CO)_4$. The Fe-H distance (1.1A) was calculated assuming a tetrahedral H-Fe-H bond angle (59).

At this point it seems desirable to evaluate the available data on transition metal-hydrogen bond distances. Regular covalent M-H bond distances are present in $[HRh(CO)(PPh_3)_3]$ (17) and in K_2ReH_9 (115). The latter compound was advantageously studied by neutron diffraction. Refinements resulted in an average Re-H distance of 1.68 $\pm$ 0.01A.

REPORTED STRUCTURES



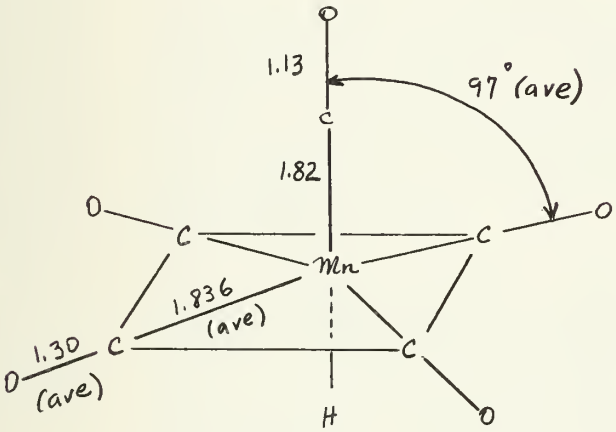
ANGLES

P_1-Rh-P_2*	115.8°	OC−Rh−P_1	94.8°
P_2-Rh-P_3	120.6	OC−Rh−P_2	103.8
P_2-Rh-P_1	94.8	OC−Rh−P_3	98.0

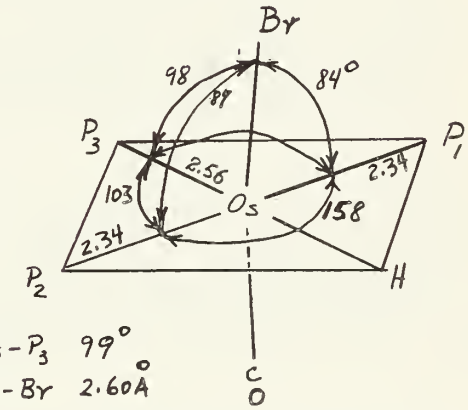
OC−Rh−P_3 170 (PLANE NOT SPECIFIED BY AUTHORS)

* NUMBERING OF THE P ATOMS IS ASSUMED.

$[HRh(CO)(PPh_3)_3]$ (17)

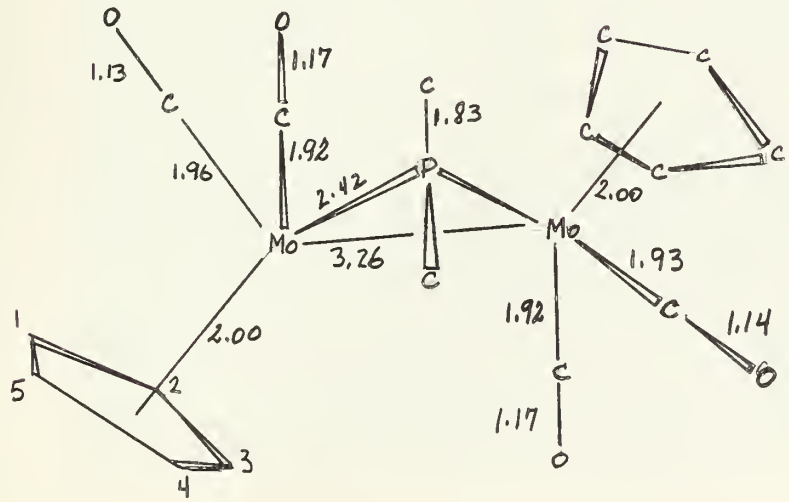


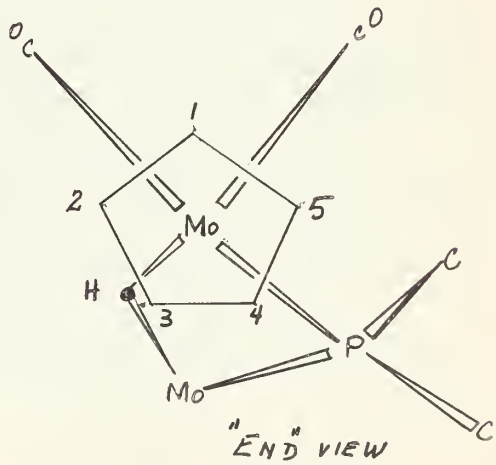
$[HMn(CO)_5]$ (31, 32)



P_1-Os-P_3 99°
Os−Br 2.60Å

$[HOs(CO)Br(PPh_2)_3]$ (33)





$[(\pi\text{-}C_5H_5)_2Mo_2H(PMe_2)(CO)_4]$ (34)

The Rh-H distance (1.72A), on the other hand, was obtained from x-ray diffraction data (covalent radii are 1.43A for Rh(60) and 0.30A for H(61)). Refinements here resulted in a final R factor of 7.7% (Rh anisotropic refinement). Since the large phenyl groups in $[HRh(CO)(PPh_3)_3]$ lock the structure into place, the other isotropic refinements seem justified. These appear to be reliable data in support of a regular covalent M-H distance.

In contrast to the above evidence, some data appear to favor a M-H bond distance very much shorter than the sum of covalent radii. These distances are based on information obtained on the molecules $HCo(CO)_4$ (49), $H_2Mo(C_5H_5)_2$ (116) and $H_2Fe(CO)_5$ (59).

In the first of these, $HCo(CO)_4$, a ca. 1.2A Co-H distance is concluded and based on the criterion of maximum total overlap between H, Co and C. However, this distance is not very certain because 1) the Co in the $Co(CO)_4$ portion is considered to be in a perfectly Sp^3 hybridized state; 2) the proton is considered to be attached to the metal via the unmixed $3d_{z^2}$ orbital of Co; 3) the uncertainty in the Slater exponents in Co.

In contrast to most publications on crystallographic results, the information about $H_2Mo(C_5H_5)_2$ appears to be of a preliminary nature. The Mo-H distance is 1.2A with an uncertainty of $\pm$ 0.2A, it was indicated (116), and is based on two-dimensional x-ray data. No anisotropic refinement was carried out, and the final R factor was 9.8%.

As mentioned above, the H-H distance in $H_2Fe(CO)_4$ was obtained from broad line NMR of the powder sample at 20°K. The intramolecular H-H distance was calculated to be 1.88 $\pm$ 0.05A. The two H atoms were considered equivalent (one proton NMR line in liquid $H_2Fe(CO)_4$ (26)) and therefore the H-Fe-H angle different from 90°, in contrast to the requirements of an earlier model (117) which placed one proton on a lobe of pure $3d_{x^2-y^2}$ and the other one on the $3d_{z^2}$ orbital of Co. The H-Fe-H angle was then considered to be between a tetrahedral one and ca. 125°. Over this range of angles, one can compute Fe-H distances of 1.15A (109°28') and 1.06A (125°44') with a knowledge of the 1.88A H-H distance. While suitable structures can be proposed for these angles, these authors (59) point out that "it is impossible to be precise regarding the H-Fe-H angle upon which the estimation of the Fe-H distance depends". For this reason the estimated Fe-H distance is 1.1A. The broadening effect from Fe^{57} (I = 1/2) in the H_2Fe part of the molecule was not considered in this work and intermolecular broadening neglected.

In view of these above data available on the transition-metal-hydrogen bond distances, it appears that the more direct and complete studies favor a regular covalent M-H distance.

2. Vibrational Spectroscopy. In general, terminal CO groups absorb in the range of 2000 to 2100 cm^{-1}, bridging ones between 1800 to 1900 cm^{-1}. The M-H stretching bond often occurs at approximately 1900 cm^{-1}.

The vibrational spectrum of $HCo(CO)_4$, for example, has been the subject of many interpretational studies (39, 40, 41, 42, 43, 44, 45, 46). The tetrahedral position of the CO groups has been assumed with the hydrogen attached 1) to the metal on a C_3 axis (43, 44) or 2) to an oxygen colinear (35) or bent (40, 47) to the MCO axis. The best analysis of its vibrational spectrum favors the H lying on the C_3 axis of the molecule and attached to the metal (44) which is in agreement with conclusions drawn from other investigations. The band at 1934 cm^{-1} is assigned to the Co-H stretching mode (2.22×10^5 dynes / cm). The band at 704 cm^{-1} corresponds to the Co-H bending motion. In addition, the following modes have been assigned (44): The C-O stretching fundamentals (2122, 2062, 2043 cm^{-1}), the M-C-O bending modes (541, 467 cm^{-1}) and Co-(CO) stretching frequencies (403, 330 cm^{-1}). A normal coordinate analysis has not as yet been attempted to arrive at a reasonable force field.

The structure of $[HFe(CO)_4]^-$ (isoelectronic with $HCo(CO)_4$ is also of C_{3v} symmetry on the basis of its Raman spectrum (50).

Several authors have concluded a C_{4v} symmetry for $HMn(CO)_5$ (40, 51). This is in agreement with the $Mn(CO)_5$ skeletal structure in the solid state (see above). The analogous $HRe(CO)_5$ and $DRe(CO)_5$ exist and two bands at 1832 and 1318 cm^{-1} were assigned to the Re-H and Re-D stretching vibrations (52).

These and other vibrational frequencies and their assignments appear in Table III below.

Polynuclear carbonyl hydrides have received less attention even though the use of local symmetry in analyzing their vibrational spectra simplifies the problem (53). The spectrum of the $[HRe(CO)_4]_3$ trimer was interpreted by Kaesz et al. in this manner (54). The molecule is of D_{3h} symmetry. The absence of a Re-H stretching frequency favors the structure with the H atoms placed symmetrically between Re atoms and in the plane of the latter.

Band assignments involving the CO parts of the molecules can be made by applying the approximations of Orgel (55) and Cotton (56) (see reference 57 for comments).

3. UV-Visible Spectral Data. The position of H in the spectrochemical series is between those of H_2O and NH_3. The following is an order of increasing ligand field strength: $I^- < Br^- < Cl^- < OH^- < H_2O < H^- = NCS^- < NH_3 < NO_2^-$. This sequence has been concluded from the location of ν_{max} of d-d bands observed in the spectra of three series of compounds (58). One series is that of Table IV.

4. NMR Spectroscopy. Several authors have reported proton chemical shifts (or τ values) of carbonyl hydrieds. These shifts are large and several are presented in Table V below. They are invariably to the high-field side of TMS. In fact, in the absence of paramagnetic species, the presence of this high-field band is taken as being diagnostic of the transition metal-hydrogen bond.

An NMR application in elucidating molecular symmetry is the work on $[HRuCl(CO)(PEt_2Ph)_3]$. The compound was prepared, and the usual high-field band (τ = 17.1) was observed in the proton NMR spectrum. This band is split into two triplets (1:2:1) by P-H coupling as follows. The P trans to the H atom gives rise to the larger coupling constant (J_{H-P}=107 cps), and a doublet is expected. However, each component of this doublet is split into a triplet by the remaining two P nuclei (J_{H-P} = 24 cps). This is interpreted to mean that the H and three P atoms are all in the same plane. The Br and CO ligands are above and below this plane.

Several theories have attempted to account for the high field shifts. One qualitative explanation was that the proton is buried in a non-bonding metal d-orbital. However, this is not plausible in view of the regular covalent Rh-H interatomic distance recently found (see above) in $[HRh(CO)(PPh_3)_3]$.

The second qualitative model assumes the H to be hydride-like. Even a -1 charge on H, however, cannot account for a τ value of 40, as τ = 5 for the H^{-1} ion (36).

Wilkinson et al. suggested that paramagnetic circulation at the metal atom, in addition to the local diamagnetic shielding at the hydrogen, would be experienced as a diamagnetic effect at H and account for the proton shift at high field. This explained the proton chemical shift in HI earlier (62).

Two quantitative treatments resulted from this latter suggestion. The first one is that of Stevens, Kern, Lsher and Lipscomb (1, 48). The more general model, however, is that of Buckingham and Stephens (36, 63). Both theories evaluate the contribution of the metal atom to the proton chemical shift and start with the Ramsey formula (62).

Buckingham and Stephen arrive at the general expression

$$\sigma^{total} = \sigma_d^{total} + \frac{1}{3}(\sigma_{xx}^{p} + \sigma_{yy}^{p} + \sigma_{zz}^{p}),$$

where $\sigma_d^{total} = \frac{e^2}{3mc^2} \left(o \left| \sum_j \frac{r^2_{Hj} + RZ_{Hj}}{r^3_{Hj}} \right| o\right)$

and refers to the "diamagnetic" contribution and where, for example,

$$\sigma_{xx}^{p} = \frac{e^2}{2m^2C^2} \sum_{n \neq o} (E_n - E_o)^{-1} \left\{ \left(o \left| \sum_j l_{MZj} \right| n\right) \cdot \left(n \left| \sum_K r^{-3}_{HK}\, l_{HxK} \right| o\right) + \text{Complex conjugate} \right\}$$

refers to part of the "paramagnetic" contribution to the total shielding constant.

With the Lipscomb model one evaluates only the diamagnetic contribution and neglects the paramagnetic term entirely. Its success, therefore, can only be attributed to σ^d being small in the several carbonyl hydrides considered.

In the more general treatment of Buckingham both diamagnetic and paramagnetic terms are evaluated. In these calculations only the first term in the above summation is retained and E_n taken from the lowest energy d-d transitions. Other parameters are R(M-H distance) and Slater's k ($\chi_r = Nr^{n-1} e^{-kr}$). It is predicted that the paramagnetic contribution is the largest by far in the total shielding ($R = 2$ a.u., $k \cong 3$, $E_1 - E_o = 25{,}000\ cm^{-1}$ for octahedral complexes).

Calculated shifts (both σ^d and σ^p) by Buckingham and Stephens for some octahedral complexes (<u>cis</u>-MX_4H_2, <u>trans</u>-MX_4YH, <u>trans</u>-MX_4H_2, MX_5H and MH_6) are much too low at M-H distances calculated from ordinary covalent radii. They therefore base their calculations on shorter M-H bond distances. However, the source of the discrepancy may lie in the approximate wave functions. It is very significant that the calculated σ^p is always about five times larger than σ^d for all reasonable values of k and R.

IV. Conclusion

It is evident that synthetic attempts have been quite successful in this area of inorganic chemistry. Table I, however, implies that many more compounds are still to be made. Their chemistry is also to be worked out more fully. Additional diffraction data are definitely needed to establish trends in structure. The latter information would then certainly make the quantitative interpretations of the data less approximate.

Table I. Reported Compounds

Vanadium Species	References	Chromium Species	References
$[HV(CO)_6]$	64	$[H_2Cr(CO)_5]$	65, 66
$[HV(CO)_5(PPh_3)]$	64	$[HCr(CO)_5]^-$	67,68,69,70,66
		$[(C_5H_5)Cr(CO)_3H]$	3, 4, 5, 1
		$[(C_6H_5CH_3)Cr(CO)_3H]^+$	9
		$[HCr_2(CO)_{10}]^-$	70,71,72,6
		$[HCr_2(CO)_6(OH)_3]^=$	73
		$[HCr_2(CO)_6(CH_3O)]^=$	73

Molybdenum Species	References	Tungsten Species	References
$[(C_5H_5)Mo(CO)_3H]$	3, 5	$[(C_5H_5)W(CO)_3H]$	3,5
$[HMo_2(CO)_{10}]^-$	6,74,1	$[HW_2(CO)_6(OH)_3]^=$	78
$[HMo_2(CO)_6(OH)_3]^=$	75	$[HW_2(CO)_6(C_5H_5)_2]^+$	9
$[H_3Mo_2(CO)_9(OH)_3]$	75	$[HW_3(CO)_9(OH)(OCH_3)(CH_3OH)]^{\equiv}$	78
$[HMo_2(CO)_6(C_5H_5)_2]^+$	9	$[H_2W_2(CO)_6(H_2O)_2 \cdot C_6H_6]$	78
$[HMo_2(CO)_4(PMe_2)(C_5H_5)_2]$	76, 77	$[H_4W_4(CO)_{12}(H_2O)_4]$	78
		$[H_4W_3(CO)_9(H_2O)(OH)_2] \cdot 3H_2O$	79
		$[H_4W_3(CO)_9(H_2O)(OH)_2]$ anhyd.	79
		$[H_2W_3(CO)_9(OH)_2(H_2O)]^=$	79
		$[HW_3(CO)_9(OH)_2(H_2O)]^{\equiv}$	79
		$[H_4W_3(CO)_9(OH)(OCH_3)(CH_3OH)]$	79
		$[H_3W_3(CO)_9(OH)(OCH_3)(CH_3OH)]^-$	79
		$[H_3W_2(CO)_6(OH)_3]$	79

Manganese Species	References	Technitium Species	References
$[HMn(CO)_5]$	80, 13	$[HTc(CO)_5]$	87
$[DMn(CO)_5]$	81, 82	$[HTc(CO)_4]_3$ (?)	88
$[HMn(CO)_4(PR_3)]$	83		
$[H_2Mn_2(CO)_9]$	84		
$[HMn(CO)_4(PPh_3)]$	85		
$[HMn(CO)_4(PEt_3)]$	85		
$[HMn(CO)_4(P(C_6H_{11})_3]$	85		
$[HMn(CO)_4(P(OC_6H_5)_3)]$	85		
$[HMn_2(CO)_8(PPh_2)]$	86		

Rhenium Species	References	Iron Species	References
$[HRe(CO)_5]$	89	$[H_2Fe(CO)_4]$	92,93
$[HRe(CO)_4]_3$	7	$[HFe(CO)_4]^-$	94
$[(C_5H_5)_2Re(CO)_2H]$	90	$[HDFe(CO)_4]$	82
$[HRe_2(CO)_8O_2]$	91	$[HFe(CO)_3(PPh_3)_2]^+$	9
		$[HFe(CO)_5]^+$	118
		$[(C_5H_5)Fe(CO)_2H]$	96,95,18
		$[(C_5H_5)_2Fe_2(CO)_4H]^+$	9
		$[(C_5H_5)_2Fe_2(CO)_2(PPh_2)H]$	97
		$[(C_5H_5)_2Fe_2(CO)_2(PMe_2)H]$	76
		$[H_2Fe_2(CO)_9]$	98
		$[H_2Fe_3(CO)_{11}]$	98
		$[HFe_3(CO)_{11}]^-$	98
		$[H_2Fe_4(CO)_{13}]$	99

Ruthenium Species	References	Osmium Species	References
$[(C_5H_5)Ru(CO)_2H]$	19	$[HOs(CO)Cl(PEt_2Ph)_3]$	100
$[(C_5H_5)Ru(CO)_2D]$	19	$[HOs(CO)Cl(PPh_3)_3]$	21, 24
$[HRu(CO)Cl(PPhEt_2)_3]$	22, 23	$[DOs(CO)Cl(PPh_3)_3]$	21, 24
$[HRu(CO)Cl(PPh_3)_3]$	21	$[HOsBr(CO)(PPh_3)_3]$	21, 24
$[HRu(CO)Br(PEt_2Ph)_3]$	23	$[DOsBr(CO)(PPh_3)_3]$	21, 24
$[HRu(CO)I(PEt_2Ph)_3]$	23	$[HOs(CO)Cl(AsPh_3)_3]$	24
		$[DOs(CO)Cl(AsPh_3)_3]$	24
		$[HOs(CO)Br(AsPh_3)_3]$	24
		$[DOs(CO)Br(AsPh_3)_3]$	24

Cobalt Species	References	Rhodium Species	References
$[HCo(CO)_4]$	101,102,103,11	$[HRh(CO)_4]$	12
$[DCo(CO)_4]$	82	$[HRh(CO)(PPh_3)_3]$	17, 30, 105
$[HCo(CO)_3PPh_3]$	104		
$[HCo(CO)_3(P(OC_6H_5)_3)]$	15		

Iridium Species	References	Nickel Species	References
$[HIr(CO)_4]$	106	$[H_2Ni_4(CO)_9]$	111
$[HIr(CO)(PPh_3)_3]$	30,107,105	$[HNi_4(CO)_9]^-$	10,112,113,111,114
$[H_2Ir(CO)Cl(PPh_3)_2]$	108	$[HNi_2(CO)_9]^-$	113
$[D_2Ir(CO)Cl(PPh_3)_2]$	108	$[H_2Ni_2(CO)_6]\cdot 4NH_3$	14, 16
$[HIr(CO)Cl_2(PPh_3)_2]$	108, 109	$[H_2Ni(CO)_3]$	38
$[HIr(CO)Cl_2(PPhEt_2)_2]$	110		
$[H_2Ir(CO)Cl_2(PPh_3)_3]Cl$	8		
$[H_2Ir(CO)Br(PPh_3)_2]$	109		

Table II. Melting Points and Colors of Some Carbonyl Hydrides

Compound	m.p. (°C)	Color
$[HCo(CO)_4]$	-26	yellow
$[H_2Fe(CO)_4]$	-70	yellow
$[HMn(CO)_5]$	-24.6	colorless
$[HRe(CO)_5]$	100	colorless
$[(C_5H_5)Cr(CO)_3H]$	57	yellow
$[(C_5H_5)Mo(CO)_3H]$	54	light yellow
$[(C_5H_5)W(CO)_3H]$	69	lemon yellow
$[(C_5H_5)Fe(CO)_2H]$	-10	yellow
$[HRh(CO)_4]$	-12	yellow
$[HRuCl(CO)(PEtPh)_3]$	100	white
$[HRuBr(CO)(PEtPh)_3]$	110-113	white
$[HRuI(CO)(PEtPh)_3]$	141-143	white
$[HOsCl(CO)(PPh_3)_3]$	179	colorless
$[HOsBr(CO)(PPh_3)_3]$	172	colorless
$[HOsCl(CO)(AsPh_3)_3]$	200	colorless
$[HOsBr(CO)(AsPh_3)_3]$	195	tan

Table III. Vibrational Frequencies (C-O, M-H, M-D) of Some Carbonyl Hydrides

Compound	ν_{M-H}, cm^{-1}	ν_{M-D}	ν_{CO}	Reference
$[HRuCl(CO)(PPh_3)]$	2020	1457	1916 1916	21
$[HRuCl(CO)PEt_2Ph)_3]$	1880		1910	23
$[HOsCl(CO)PEt_2Ph)_3]$	2100	1505	1899 1880	21
$[HOsBr(CO)(PEt_2Ph)_3]$	2105	1509	1902 1886	21
$[(C_5H_5)Mo(CO)_3H]$	--	--	2030 1949 1913	5
$[(C_5H_5)W(CO)_3H]$	--	--	2020 1929 1913	5
$[HPh(CO)(P(Ph)_3)_3]$	2004	--	1926	30
$[HIr(CO)(PPh_3)_3]$	2068	--	1930	30
$[HRe(CO)_5]$	1832	1318	--	52
$[HCo(CO)_4]$	1934		2122, 2062 2043	44

Table IV. The Electronic Spectra of trans - $[Rhen_2XCl]^+$ Complexes (58)

Complex Ion	$^1A_{2g}$, $^1E_g \leftarrow {}^1A_{1g}$	$^1B_{2g}$, $^1Eg \leftarrow {}^1A_{1g}$
$[Rhen_2ICl]^+$	22, 730 cm^{-1}	---
$[Rhen_2BrCl]^+$	24, 210	---
$[Rhen_2ClCl]^+$	24, 630	34, 970
$[Rhen_2(H_2O)Cl]^{+2}$	26, 180	35, 710
$[Rhen_2HCl]^+$	27, 400	---
$[Rhen_2(NCS)Cl]^+$	27, 550	---
$[Rhen_2(NH_3)Cl]^{+2}$	29, 240	36, 360
$[Rhen_2(NO_2)Cl]^+$	32, 360	---

Table V. τ-Values from Proton NMR Spectra of Some Carbonyl Hydrides

Compound	τ-Value for M-H Proton (TMS = 10)
$HMn(CO)_5$	17.5
$H_2Fe(CO)_4$	21.1
$HCo(CO)_4$	20.0
$HFe_3(CO)_{11}^-$	24.9
$H_2Fe_3(CO)_{11}$	24.9
$HCr(CO)_3(C_5H_5)$	15.95
$HMo(CO)_3(C_5H_5)$	15.65
$HW(CO)_3(C_5H_5)$	17.65
$HFe(CO)_2(C_5H_5)$	20.0

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Errata

Page	Printed Line	Corrected Reading
86	6	"...<u>with Basic Alcohol</u>."
87	19	"...$[(C_5H_5)_2Mo_2H(CO)_4(PMe_2)]$."
89	2	"...are <u>ca</u>. 1.27A..."
91	5 (from bottom)	"...Kern, Lohr, Jr.,..."
92	11	"...σ^{p}..."
92	17	"...$\psi_r = Nr^{n^*-1} e^{-kr}$..."

RECENT CHEMISTRY OF PHOSPHOROCHLORIDES

V. Alan Mode May 4, 1965

Introduction

The recent interest in phosphorus chemistry has developed along two lines: (a) the study of phosphorus compounds by analogy to carbon chemistry and examination of the biochemical importance of organo-phosphorus compounds; (b) the study of phosphorus compounds as non-aqueous solvent systems for inorganic chemistry. This seminar will deal with some recent studies that developed from the non-aqueous solvent work and has employed the very similar behavior of four-coordinate phosphorus and analogus carbon compounds.

$POCl_3$ Self-ionization

The use of $POCl_3$ as a non-aqueous solvent is extensively reported in the literature. In many cases, the observed chemistry has been explained by extension of the auto- or self-ionization concepts from aqueous systems:

$$2H_2O \rightleftarrows H_3O^+ + OH^- \qquad \text{(I)}$$

$$POCl_3 \rightleftarrows POCl_2^+ + Cl^- \qquad \text{(II)}$$

In 1957, Lewis and Sowerby (1) reported experiments which cast considerable doubt on the importance of the ionization shown in equation (II). They were able to explain the observed radiochemical exchange reactions on the basis of a five-coordinate intermediate or transition state which did not involve self-ionization of $POCl_3$.

Five-Coordinate Phosphorus

A five-coordinate state of phosphorus is not unexpected. Compounds of the type PA_5 (e.g. PCl_5) have been known and studied for years. Substitution reactions in four-coordinate phosphorus have been shown to occur via a five-coordinate state (2,3,4). It was further shown by Green and Hudson (5) that substitution and exchange reactions proceed by the same mechanism. During racemization of methyl ethyl-phenylphosphinate, methoxide exchange was also determined. The rate of racemization was twice the rate of exchange and the overall exchange was second order as would be predicted if the mechanism was one of a five-coordinate transition state where the phosphorus compound was undergoing a "Walden"-type inversion.

The possibility of a stable five-coordinate intermediate has been eliminated (6,7). While this work does not define a specific tran-sition configuration, it did show that the life time of the five-coordinate state was much less than the period required for proton migration between similar oxygens in the compound.

The numerous studies of nucleophilic displacement reactions on phosphorus have been reviewed and discussed by G. D. Shier (8). As these studies have been conducted in hydroxylic solvents, the possibility of large contributions from solvation of the ground and transition state make interpretation quite difficult. While a number of authors have attempted to ascertain the relative importance of bond making vs. bond breaking, solvation effects could dominate and make any statements or conclusions highly questionable.

Recent Studies

In recent work, it has been possible to select either a non-polar solvent (tetrachloroethylene), or a non-hydroxylic solvent (1,2-dichloroethane), and in this way to minimize the effects of solvation. In the exchange of chloride-36 with $RPOCl_2$, reactant and product are the same chemical compound, and the formation of a symmetric transition state eliminates the effects of asymmetric charge distribution and serves to further reduce solvation effects.

Conjugative as well as inductive effects have been found to be important in explaining the ground state properties of four-coordinate phosphorus as well as in the five-coordinate transition state. However, the relative importance of each effect changes in going from the ground state to the transition state.

Enthalpies of phenol-phosphoryl adduct formation are found to decrease in the order:

$$R = (CH_3)_2N\frown C_6H_5(3.4) > CH_3(3.3) > CH_3O\ (3.1) > C_6H_5O\ (3.0) > Cl\ (2.5) \qquad \text{(III)}$$

where the data in parantheses is the enthalpy in kcal/mole. Conjugative effects are shown to be of great importance and this has been confirmed by examination of the previously published NQR data (9).

By comparison, the rate of chloride-36 exchange with $RPOCl_2$ is found to decrease in the order:

$$R = C_6H_5\ (1.07) > CH_3\ (0.84) > Cl\ (0.41) > CH_3O\ (0.36) > C_6H_5O\ (0.0029) \qquad \text{(IV)}$$

where the data in parantheses is the second order rate constant at -30.0°. Here the inductive withdrawal of electron density by the groups in the trigonal plane of the five-coordinate transition state (a trigonal bipyramid) is found to be important (10).

It would be helpful if NMR studies could distinguish inductive vs. conjugative contributions; however, secondary effects have limited the interpretation of recent P-31 NMR studies. It is hoped that

further examination of phosphorus chemistry will lead to new understanding. Certainly this is a fruitful area for both organic and inorganic chemistry.

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SOME APPLICATIONS OF GAS CHROMATOGRAPHY TO THE SEPARATION AND IDENTIFICATION OF METAL COMPOUNDS

James Murphy May 25, 1965

INTRODUCTION

Since the first applications of gas-liquid chromatography to the separation and identification of metal compounds in 1959, this technique has proven itself to be very useful and versatile. Very many volatile metal compounds are highly reactive, toxic, or explosive, and it is therefore convenient to be able to handle them in an inert atmosphere and in small quantities, which is normally the case in gas chromatography. They are often prepared by reactions which lead to a very complex mixture of products, so that an efficient technique is required to separate them. Moreover, gas chromatographic results can often be used to identify a substance, even when this substance has never been isolated before.

DIFFICULTIES ENCOUNTERED IN THE USE OF GAS CHROMATOGRAPHY WITH METAL COMPOUNDS.

Since the vapor pressure of most metal compounds is relatively low, either high temperature or low pressure are necessary for handling the compounds in the vapor phase and for the application of gas chromatography to their separation and determination. These conditions generally decrease the efficiency of a column and severely limit the possibilities for the stationary liquid phase (1). Instruments for gas chromatography at up to 500°C are commercially available. Other instruments for work from 500°C to 1000°C have been reported (1)(2). Several liquid phases have been used in the high temperature region. These include the silicones and polyesters (1) up to 300°C and fused salt eutectics at higher temperatures (3).

The thermal stability of the compounds at high temperatures also must be considered. A restriction on the choice of materials for the instrument, solid support, and liquid phase is imposed by the reactivity of some of the compounds.

POSSIBLE COMPOUNDS TO WHICH GAS CHROMATOGRAPHY MIGHT BE APPLIED

The following table lists the boiling points of several classes of metal compounds.

BOILING POINTS OF VARIOUS METAL COMPOUNDS

COMPOUND	BOILING POINT (°C)
$Sb(CH_3)_3$	80.6
$Bi(CH_3)_3$	110
$Re(CH_3)_3$	60
$Fe(CO)_5$	102.8
$Ni(CO)_4$	43
$W(CO)_6$	175
$Be(C_5H_7O_2)_3$	270
$Al(C_5H_7O_2)_3$	314-350
$Cr(C_5H_7O_2)_3$	340
SiH_4	-14.5
B_2H_6	-92.5
GeH_4	-90.0
$AsCl_3$	130.2
$GeCl_4$	83.1
$SiCl_4$	57.6
UF_6	56
IrF_6	53
MoF_6	35

The relatively low boiling points of these classes of compounds indicate the possibility of their separation and identification by gas chromatography, and this technique has been developed for use with metals, metal carbonyls, metal complexes, metal hydrides, and metal halides.

METALS

A partial gas chromatographic separation of the constituents of a zinc-cadmium alloy was obtained on a column containing 20% LiCl on sea sand at 620°C (4).

METAL CARBONYLS

Compound	Reference
$W(CO)_6$	5
$Cr(CO)_6$	6
$\pi CpMn(CO)_3$	6

Hutchinson studied mixtures of metal carbonyls (5) including those of tungsten, molybdenum, and chromium, and concluded that only $W(CO)_6$ was suitable for gas chromatographic separation, but other workers (6) had previously shown that $Cr(CO)_6$ could be effectively separated and purified by gas chromatography.

ORGANOMETALLIC COMPOUNDS

Many organometallic compounds have been separated, identified, and purified using gas chromatography techniques.

Compounds	Reference
Methyl Ferrocene	5
R-Hg-Br(R=CH_3, C_2H_5, nC_3H_7, etc.)	7
$Si(Me)_4$, $Ge(Me)_4$, $Sn(Me)_4$, $Pb(Me)_4$	8
$Pb(Et)_4$, $Ge(Et)_4$	6
$Pb(Me(_4$, $Pb(Me)_3Et$, $Pb(Me)_2Et_2$, $Pb(Me)Et_3$, $Pb(Et)_4$	12, 13, 14
SiR_4 and Halogen Derivatives	16, 17, 18, 19, 20
$Si_2(Et)_6$, $Ge_2(Et)_6$, and $SiGe(Et)_6$	21
SnR_4, and Halogen Derivatives	22, 23, 26, 9
Fluoroalkyl tin	24, 25
SnR_3H, R_2SnH_2	26
Alkyl borane and diborane	27, 28
Alkyl substituted borazoles	29, 30
Organo arsenic	31, 32
Organo bismuth	33

The separation of the organometallic derivatives of the Group IVA elements has been extensively studied. Abel, et.al. (8) found that plots of molecular weight and boiling point vs. log retention time were linear for the tetramethyl derivatives of silicon, germanium, tin, and lead, and thus completely analogous to purely organic systems.

Gas chromatography has also been used as an analytical technique for the determination of tetraethyl lead in gasoline (10,11).

Pollard, et.al. (15) used gas chromatography to separate trimethyl silyl ethers and trimethyl thiosilyl ethers, to study the pyrolysis products of the methyl chlorosilanes, and rearrangement products involving the interchange of alkyl groups on silanes using $AlCl_3$ as a catalyst. The pyrolysis products of methyl chlorosilanes were also studied by Fritz and co-workers (16,17). Several quantitative determinations of alkyl silanes have also been performed (19,20)

Phillips and co-workers (29,30) have extensively studied alkyl substituted borazoles. The emphasis of the articles is on the identification of borazoles by gas chromatographic retention data.

They have shown that once a compound has been associated with its characteristic retention time in the chromatogram, it may generally be identified again when it appears as a result of another reaction. From retention evidence, they have proposed the existence of ortho-para type isomers in the alkyl substituted borazoles.

The increased volatility of the perfluoroalkyl arsenic compounds compared with their alkyl analogs was noted by Gudzinowics, et.al. (31,32), even though a higher molecular weight group had been incorporated, ie. the retention time decreased. The same effect was noted by Sievers, et.al. in the metal complexes of acetylacetone and hexafluoroacetylacetone (34).

METAL COMPLEXES

The separation of metal complexes by gas chromatography has been limited to certain acetylacetonates (Acac), trifluoroacetylacetonates (TFA), and hexafluoroacetylacetonates (HFA).

Compound Type	Examples (M)	Temp.	Reference
$M(Acac)_x$	Be(II), Sc(III), Zn(II)		35
	Be(II), Al(III), Cu(II)	150-200°C	34,37
	V(IV), Cr(III)		
$M(TFA)_x$	Be(II), Al(III), In(III), Cu(II), Fe(III), Rh(III), Zr(IV), Hf(IV)	100°-150°C	34,37
$M(HFA)_x$	Cr(III), Rh(III) - 30°C →		34,37

Sievers et.al. (34,37,77) were able to separate the cis-trans isomers of $Cr(TFA)_3$ and $Rh(TFA)_3$, but found it impossible to separate the d,l isomers of $Cr(TFA)_3$ using a column with 1% dibutyl-d-tartrate on glass beads, although a partial resolution had been obtained earlier (38) using gas-solid chromatography with d-quartz as the solid phase.

The possibility of using gas chromatography of complexes for quantitative analysis of metals has been suggested by several workers (37,39,41,42,77). Several new detectors have been developed (43,44,45) which extend the limits of detection to 3.3×10^{-11}g for $Cr(HFA)_3$ and 4.8×10^{-10}g for $Al(HFA)_3$ and also to increase the sensitivity for one element in the presence of another.

METAL HYDRIDES:

The gas chromatography techniques for metal hydrides has been extensively studied.

Compound Type	Reference
Silanes	17,46,47,48,49
Germanes	49,50,51
Silicogermanes	30,52
Boranes	53,54,55,56,57,58,59,60,61

Feher et.al. (48) have found that twenty-six silanes in one mixture could be chromatographically separated. Drake and coworkers (50,51) used gas chromatography to separate a mixture of germanium hydrides, and those higher than tetragermanes were identified solely on the basis of their chromatographic retention times. Phillips et.al. (30,52), in their studies on mixed silicon-germanium hydrides, have shown that, in certain select cases, the retention time for a compound may be predicted on the basis of retention times for the components of the compound.

A rapid quantitative determination of B-H bonds in a molecule utilizing gas chromatography has been developed (55,56). Kinetic data on the pyrolysis of diborane (57), the composition of mixtures obtained from the hydrogen reduction of BCl_3 (15,8), and the identification of products from radiation induced reactions of penta and deca borane have been obtained using gas chromatography (60). A continuous preparative gas chromatograph for the purification of pentaborane (20-40g/hr) has been developed (61).

METAL HALIDES

Gas chromatography of the metal halides is somewhat more difficult than that of the compounds previously discussed. The high boiling points and the extreme reactivity of these compounds necessitates the use of special types of apparatus for their separation.

BOILING POINTS OF SOME METAL CHLORIDES

Metal	B.P.°C	Metal	B.P.°C
Boron(III)	13	Niobium	246
Silicon	58	Tantalum	232
Germanium	86	Gold(III)	265 (subl.)
Tin(IV)	114	Molybdenum(V)	268
Arsenic(III)	130	Tungsten(V)	275
Titanium(IV)	136	Mercury(II)	304
Vanadium(V)	149	Hafnium	317
Antimony(V)	172	Iron(III)	319
Aluminum	178(subl.)	Zirconium	331
Gallium	215	Tungsten(VI)	337
Antimony(III)	220		

GAS CHROMATOGRAPHIC SEPARATIONS OF METAL ~~HYDRIDES~~ HALIDES

Compounds	Liq. Phase	Reference
$SnCl_4$, $TiCl_4$	n-hexadecane	63
$TiCl_4$, $NbCl_5$, $TaCl_5$	n-alkanes	64,65
$AsCl_3$, $AsCl_5$, $SbCl_3$	fused	66
$SbCl_5$, $SnCl_4$, $TiCl_4$	$BiCl_3$ - $PbCl_2$ eutectic	
UF_6	-	72,73,74,75,76

Two general types of liquid phases have been used for the separation of metal halides, organic phases (62,63,64,65) and fused salts (3,66,67). The use of organic liquids is limited in that it reacts with the metal halides (62,64,65,71), but some compounds have been separated with theseliquids as partitioning agents.

Fused salt liquid phases must be chosen so that they have a low vapor pressure at the temperature of the column and so that they have a common anion with that of the solute molecules in order to minimize the possibility of undesirable reactions on the column.

Tivin (66) has shown that in some cases one may easily analyze mixtures of oxidation states, since the chlorides have different boiling points.

Tadmor has noted (69,70,71) that isotopic exchange between metal chlorides and a Cl^{36} labeled solid phase can occur, and pure labeled compounds can be obtained in this manner. $FeCl_3$ will also undergo isotopic exchange with a Fe^{59} labeled column containing neutron irradiated FeS as the solid phase.

CONCLUSION:

Gas chromatography has proven itself to be a valuable tool for the identification, purification, and separation of many types of metal compounds, but much of this field remains yet to be explored. With the development of new instruments and techniques, it should prove to be even more versatile in the future.

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